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"The first and most important step towards success is to believe that we can succeed."

Quantum Chemistry

* Einstein's equation : $E = mc^2$.

Planck's equation : $E = h\nu$

De-broglie equation : $h\nu = mc^2$

$$\Rightarrow \frac{hc}{\lambda} = mc^2$$

$$\lambda = \frac{h}{mc} \Rightarrow \boxed{\lambda = \frac{h}{p}} \quad \text{—(*)}$$

→ With the help of * de-broglie showed that microscopic particles show wave nature as well as particle nature.

→ When wave nature is shown by a particle, then to describe it, we have a wave equation known as schrödinger wave equation.

→ The solution of this wave equation is also known as wave function denoted by the symbol ψ.

→ For every observable in classical mechanics, there is an operator corresponding to it in quantum mechanics.

* Some operators corresponding to every observable in quantum chemistry.

(i) Observable ⇒ Position	Operator	Function
x, y, z	$\hat{x}\ \hat{y}\ \hat{z}$	Multiply.

Ex:- $\psi = e^x$

$\hat{A}\psi = \hat{x}e^x$

$\boxed{\hat{A}\psi = xe^x}$

→ eigen value.

Remember, operator is meaningless without function.
operator always operates from the left side.

* Observable — Operator

Linear Momentum

P_x

P_y

P_z

$$\boxed{\hat{P}_x = -i\hbar \frac{d}{dx} = -i\frac{h}{2\pi}\frac{\partial}{\partial x} = \frac{\hbar}{i}\frac{\partial}{\partial x} = \frac{h}{2\pi i}\frac{\partial}{\partial x}}$$

Similarily,

$$\boxed{\hat{P}_y = -i\hbar \frac{\partial}{\partial y} = -i\frac{h}{2\pi}\frac{\partial}{\partial y} = \frac{\hbar}{i}\frac{\partial}{\partial y} = \frac{h}{2\pi i}\frac{\partial}{\partial y}}$$

<u>Function</u>: Differentiate w.r.t. 'x' or 'y' or 'z' in x, y, z direction respectively and multiply by $-i\hbar / -\frac{ih}{2\pi}$

<u>Ex</u>:- <u>Gate</u>; $\psi = e^{ikx}$ and $P_x = -i\hbar\frac{\partial}{\partial x}$

we know that $\boxed{\hat{A}\psi = a\psi}$

$$\hat{P}_x\psi = -i\hbar\frac{\partial}{\partial x}\psi$$

$$= -i\hbar\frac{\partial}{\partial x}e^{ikx}$$

$$= -i\hbar . ik e^{ikx}$$

$$= -i^2\hbar k e^{ikx}$$

$$= \hbar k e^{ikx}$$

$$\boxed{\hat{P}_x\psi = \hbar k \psi}$$

Hence value of linear momentum for wave function $= \hbar k$

* Observable = Kinetic energy $\{K_x, K_y, K_z\}$

Operator = $\hat{K}_x = \frac{-\hbar^2}{2m}\frac{d^2}{dx^2} = -\left(\frac{h}{2\pi}\right)^2\frac{1}{2m}\frac{d^2}{dx^2} = \frac{-h^2}{8\pi^2 m}\frac{d^2}{dx^2}$

$$\hat{K}_y = \frac{-\hbar^2}{2m}\cdot\frac{d^2}{dy^2} = -\left(\frac{h}{2\pi}\right)^2\cdot\frac{1}{2m}\frac{d^2}{dy^2} = \frac{-h^2}{8\pi^2 m}\cdot\frac{d^2}{dy^2}$$

$$\hat{K}_z = \frac{-\hbar^2}{2m}\frac{d^2}{dz^2} = -\left(\frac{h}{2\pi}\right)^2\frac{1}{2m}\frac{d^2}{dz^2} = \frac{-h^2}{8\pi^2 m}\frac{d}{dz^2}$$

* Relation between Kinetic Energy Operator and Linear Momentum Operator.

We know that;

$$\hat{P}_x = -i\hbar \frac{\partial}{\partial x}$$

$$\hat{K}_x = \frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2}$$

$\because$ $KE = \frac{1}{2}mv^2$

$$KE = \frac{m^2v^2}{2m}$$

$$\boxed{KE = P^2/2m}$$ and $$\boxed{\hat{K}_x = \frac{\hat{P}_x^2}{2m}}$$

Proof:

$$K_x = \frac{\left(-i\hbar\frac{\partial}{\partial x}\right)^2}{2m}$$

$$\hat{K}_x = \frac{i^2\hbar^2\frac{\partial^2}{\partial x^2}}{2m}$$

$$\hat{K}_x = \frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2}$$

$$= \boxed{\hat{K}_x = \frac{-\hbar^2}{2m}\cdot\frac{\partial^2}{\partial x^2}}$$

* Observable :- Potential $\{V_x, V_y, V_z\}$

Operator :- $\hat{V}_x$, $\hat{V}_y$, $\hat{V}_z$

Function :- Multiply.

* Total Energy Operator. Total energy operator is also known as Hamiltonian operator.

It is represented by $\hat{H}$.

We know that,

$$\boxed{T.E. = K.E. + P.E.}$$

$$\hat{H}_x = \hat{K}_x + \hat{V}_x = \frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + \hat{V}_x$$

$$\hat{H}_y = \hat{K}_y + \hat{V}_y = \frac{-\hbar^2}{2m}\frac{\partial^2}{\partial^2 y} + \hat{V}_y$$

$$\hat{H}_z = \hat{K}_z + \hat{V}_z = \frac{-\hbar^2}{2m}\frac{\partial^2}{\partial^2 z} + \hat{V}_z$$

and we know that;

$$\hat{H} = \hat{H}_x + \hat{H}_y + \hat{H}_z$$

$$\hat{H} = \frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + \hat{V}_x + \frac{-\hbar^2}{2m}\frac{\partial^2}{\partial^2 y} + \hat{V}_y - \frac{\hbar^2}{2m}\frac{\partial^2}{\partial^2 z} + \hat{V}_z$$

$$\hat{H} = -\frac{\hbar^2}{2m}\left\{\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right\} + (\hat{V}_x + \hat{V}_y + \hat{V}_z)$$

and we know that

Laplacian operator $(\nabla^2) = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$

$$\boxed{\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + V}$$

* Angular Momentum Operator :-

$$\boxed{\vec{L} = \vec{r} \times \vec{P}}$$

$\vec{L}$ = Angular Momentum

$\vec{r}$ = Position

$\vec{P}$ = Linear Momentum.

and we know that;

$$\vec{r} = x\hat{i} + y\hat{j} + z\hat{k}$$

$$\vec{P} = P_x\hat{i} + P_y\hat{j} + P_z\hat{k}$$

Now;

$$\vec{L} = \vec{r} \times \vec{P} = \begin{vmatrix} \hat{i} & \hat{j} & \hat{k} \\ x & y & z \\ P_x & P_y & P_z \end{vmatrix}$$

$$= \hat{i}\{yP_z - zP_y\} - \hat{j}\{xP_z - zP_x\} + \hat{k}\{xP_y - yP_x\}$$

$$= \hat{i}\{yP_z - zP_y\} + \hat{j}\{zP_x - xP_z\} + \hat{k}\{xP_y - yP_x\}$$

$$= L_x\hat{i} + L_y\hat{j} + L_z\hat{k}$$

$$\boxed{\vec{L} = L_x\hat{i} + L_y\hat{i} + L_z\hat{k}}$$

where,

$$\boxed{\begin{aligned} \hat{L}_x &= yP_z - zP_y \\ \hat{L}_y &= zP_x - xP_z \\ \hat{L}_z &= xP_y - yP_x \end{aligned}}$$

$$L_x = yP_z - zP_y$$

$$= y\left\{-i\hbar\frac{\partial}{\partial z}\right\} - z\left\{-i\hbar\frac{\partial}{\partial y}\right\}$$

$$\boxed{L_x = -i\hbar\left\{y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right\}}$$

or

$$\boxed{L_x = \frac{\hbar}{i}\left\{y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right\}}$$

$$\boxed{L_x = \frac{h}{2\pi i}\left\{y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right\}}$$

* Let suppose we have,

operator = A^2
Function = ψ $\Rightarrow$ $\boxed{\hat{A}^2\psi = \hat{A}\hat{A}\psi}$

GATE :- $\hat{A} = \left[x + \frac{d}{dx}\right]$ find $\hat{A}^2$.

∵ We know that an operator is meaningless without a function. Hence let us consider a function, $\psi(x)$.

$$\boxed{\hat{A}^2\psi(x) = \left(x + \frac{d}{dx}\right)^2 = x^2 + \frac{d^2}{dx^2} + 2x\frac{d}{dx}}$$ —XX ये काम गलती से भी न करना.

Now,
$$\hat{A}^2 f(x) = \hat{A}\hat{A}f(x) = \hat{A}\left\{x + \frac{d}{dx}\right\}\psi(x)$$
$$= \hat{A}\left\{x\psi(x) + \frac{d}{dx}\psi(x)\right\}$$
$$= \left\{x + \frac{d}{dx}\right\}\left\{x\psi(x) + \frac{d}{dx}\psi(x)\right\}$$
$$\hat{A}^2\psi(x) = x^2\psi(x) + x\frac{d}{dx}\psi(x) + \frac{d}{dx}\overset{I}{\psi(x)}\cdot\overset{II}{x} + \frac{d^2}{dx^2}\psi(x).$$
$$= x^2\psi(x) + x\frac{d}{dx}\psi(x) + \psi(x) + x\frac{d}{dx}\psi(x) + \frac{d^2}{dx^2}\psi(x)$$
$$= x^2\psi(x) + 2x\frac{d}{dx}\psi(x) + \psi(x) + \frac{d^2}{dx^2}\psi(x)$$
$$\hat{A}^2\psi(x) = \left\{x^2 + 2x\frac{d}{dx} + \frac{d^2}{dx^2} + 1\right\}\psi(x)$$

Compairing with
$$\hat{A}^2\psi(x) = A^2\psi$$
$$\Rightarrow \boxed{A^2 = \left\{x^2 + 2x\frac{d}{dx} + \frac{d^2}{dx^2} + 1\right\}}$$

* Properties of Operators.

(i) Linearity :- Operators used in quantum chemistry are generally linear. i.e. they can be applied to a complete func as well as if a function is divided into two or more parts. If the result given by the operator in both the cases is same then the operator is said to be linear.

Ex :- Differentiation operator, Integration operator.

→ Differentiation operator.

Let $\psi = 5x^2$

and $\hat{A} = \frac{d}{dx}$

$\Rightarrow \hat{A}\psi = \frac{d}{dx} 5x^2 = 10x. \Rightarrow \boxed{\hat{A}\psi = 10x}$

Let $\psi = 3x^2 + 2x^2$

$\hat{A}\psi = \frac{d}{dx} 3x^2 + \frac{d}{dx} 2x^2 \Rightarrow 6x + 4x = 10x$ $\boxed{\hat{A}\psi = 10x}$

Hence diff. operator shows linear property.

⊛ COMMUTATOR :

Commutator is a mathematical operation b/w two operators.

Representation = $[\hat{A}, \hat{B}]$

Operation = $[AB - BA]$

If $AB - BA = 0 \Rightarrow$ Given two operation commutes with each other.

$AB - BA \neq 0 \Rightarrow$ Given two operators do not commute with each other.

→ Properties of Commutator :-

~~(i) Additional~~

(i) Antisymmetric :

$\psi(x) = x^2$

$\psi(-x) = x^2 \Rightarrow \boxed{\psi(x) = \psi(-x)}$

Given func^n is symmetric.

and if ;

$\psi(x) = x$

$\psi(-x) = -x$

$\Rightarrow \boxed{\psi(x) = -\psi(-x)}$

Given func^n is antisymmetric

Hence, $\boxed{[\hat{A}, \hat{B}] = -[\hat{B}, \hat{A}]}$ If position of operators inside the commutator brackets are changed, then the commutator shows antisymmetric property.

iii) Linearity :- $[\hat{A}, \hat{B}+\hat{C}] = [\hat{A},\hat{B}] + [\hat{A},\hat{C}]$

$$[\hat{A}+\hat{B}, \hat{C}+\hat{D}] = [\hat{A},\hat{C}] + [\hat{A},\hat{D}] + [\hat{B},\hat{C}] + [\hat{C},\hat{D}]$$

Example:-

$$[x+P_x, P_x] = [\hat{x},\hat{P}_x] + [\hat{P}_x,\hat{P}_x]$$

iii) Distributivity :-

$$[\hat{A}, \hat{B}\hat{C}] = [\hat{A},\hat{B}]\hat{C} + \hat{B}[\hat{A},\hat{C}]$$

Example,

$$[x\hat{P}_x, \hat{x}] = [\hat{x},\hat{x}]P_x + x[\hat{P}_x,\hat{x}]$$

(iv) Constant Quantity comes out of commutator bracket.

$$[a\hat{A},\hat{B}] = a[\hat{A},\hat{B}]$$

$$[a\hat{A}, b\hat{B}] = ab[\hat{A},\hat{B}]$$

Example:- $[P_x, x] = \left[-i\hbar\frac{\partial}{\partial x}, x\right] = -i\hbar\left[\frac{\partial}{\partial x}, x\right]$

(v) Self Commutation is zero.

$$[\hat{A},\hat{A}]=0 \quad \text{and} \quad [\hat{A}\,\hat{A}^n]=0$$

i.e. any operator always commutes with itself.

Ex:- GATE : Find Value of $\left[\frac{d}{dx}, \frac{d^2}{dx^2}\right]$

we know that,

$$A = \frac{d}{dx} \quad \text{and} \quad [\hat{A},\hat{A}^2]=0$$

$$A^2 = \frac{d^2}{dx^2}$$

$$\Rightarrow \left[\frac{d}{dx}, \frac{d^2}{dx^2}\right]=0$$

Ex:- $[K_x, P_x]$

$$\left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}, -i\hbar\frac{d}{dx}\right] \Rightarrow \frac{-i\hbar^3}{2m}\left[\frac{d^2}{dx^2}, \frac{d}{dx}\right] \quad \text{and} \quad \left[\frac{d^2}{dx^2}, \frac{d}{dx}\right]=0$$

$$\Rightarrow [K_x, P_x]=0$$

VI :- Two operators with multiplication operation commutes with each-other.

Eg. Position → Multiplication
P.E. → Multiplication.

$\Rightarrow$ ~~[x, p~~ $[x, V_x] = 0$
Position, Multiplication.

Ex:- Whether $\hat{A}, \hat{B}$ commutes or not when, $A = \frac{d}{dx}$ $B = x$.

First, Let us consider a func^n $\psi(x)$.

$$\left[\frac{d}{dx}, x\right]\psi \Rightarrow \left\{\frac{d}{dx}x - x\frac{d}{dx}\right\}\psi$$

$\because$ $[\hat{A}, \hat{B}]$
$\Downarrow$
$[AB - BA]$

$$= \left\{\frac{d}{dx}\underset{I}{x}\underset{II}{\psi} - x\frac{d}{dx}\psi\right\}$$

$$= x\frac{d}{dx}\psi + \psi\frac{d}{dx}x - x\frac{d}{dx}\psi$$

$$= 1.\psi$$

$$\left[\frac{d}{dx}, x\right]\psi = 1.\psi.$$

$\Rightarrow \left[\frac{d}{dx}, x\right] = 1$ Hence $\left[\frac{d}{dx}, x\right]$ do not commute with each other.

Similarily, $\boxed{\left[\frac{d}{dx}, x^n\right] = nx^{n-1}}$ Results are similar to that of diff^n but this is not the diff^n. This is commutative operation.

$\Rightarrow$ First derivative operator commutes with position operator shows similar results to differentiation.

$\because$ Commutator shows antisymmetric property,

$$\Rightarrow \left[x, \frac{d}{dx}\right] = -1.$$

Similarily, $\left[x^n, \frac{d}{dx}\right] = -nx^{n-1}$.

Example:- $[P_x, x^n] = \left[-i\hbar\frac{d}{dx}, x^n\right]$

$$= -i\hbar\left[\frac{d}{dx}, x^n\right]$$

$$= -i\hbar n x^{n-1}$$

$[\hat{A}, a] = 0$ i.e. any operator commutates with constant quantity.

i.e.

$[\hat{A}, i\hbar] = 0.$

<u>Example</u>: Solve $[x, P_x^2]$

$$= [x, P_x P_x] = [x, P_x]P_x + P_x[x, P_x]$$

$$= i\hbar P_x + i\hbar P_x$$

$$= 2i\hbar P_x$$

$$\boxed{[x, P_x^n] = i\hbar n P_x^{n-1}}$$

$\Rightarrow$ $[x, P_x^2] = 2i\hbar P_x$ $\qquad$ $[P_x^2, x] = -2i\hbar P_x$

$[x, P_x^3] = 3i\hbar P_x^2$ $\qquad$ $[P_x^3, x] = -3i\hbar P_x^2$

$[x, P_x^4] = 4i\hbar P_x^3$ $\qquad$ $[P_x^4, x] = -4i\hbar P_x^3$

* Revision of Some Formulaes:

i. $\left[\frac{d}{dx}, x^n\right] = nx^{n-1}$ $\qquad$ ii. $\left[x^n, \frac{d}{dx}\right] = -nx^{n-1}$

iii. $[P_x, x^n] = -i\hbar n x^{n-1}$ $\qquad$ iv. $[x^n, P_x] = i\hbar(nx^{n-1})$

v. $[x, P_x^n] = ni\hbar P_x^{n-1}$ $\qquad$ vi. $[P_x^n, x] = -ni\hbar P_x^{n-1}$

* Commutator of Linear Momentum:-

$$\left.\begin{array}{ll} [P_x, P_x] = 0 & [P_x, P_y] = 0 \\ [P_y, P_y] = 0 & [P_y, P_z] = 0 \\ [P_z, P_z] = 0 & [P_z, P_x] = 0 \end{array}\right\} [\hat{P}, \hat{P}] = 0$$

* Linear Momentum and Position Operator.

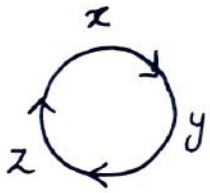
$[\hat{P}, \text{Position}] \Rightarrow$ value {some value will definitely come}

same direction

<u>Ex</u>: $[P_x, x] = -i\hbar.$

But $[P_x, y] = 0$, $[P_y, z] = 0$ } Different direction will give 0.

⊛ Commutator of Angular Momentum :-



$x \to y \to z$ {clockwise} (positive value)

$z \to y \to x$ {Anticlockwise} (negative value)

① [Angular Momentum, Position]

same direction → Always Commute.
Value = 0.

$[L_x, x] = 0$
$[L_y, y] = 0$
$[L_z, z] = 0$

Proof:- $[L_x, x] = [yP_z - zP_y, x]$

$= [yP_z, x] - [zP_y, x]$

$= y[P_z, x] - z[P_y, x]$ → Last page.

$= y(0) - z(0)$

$= 0.$

② [Angular Momentum, Position]

Different direction, never commutes, always give some value.

Ex:- $[L_x, y] = +i\hbar z$ $(x \to y \to z)$ $\quad [L_y, z] = i\hbar x$ $(y \to z \to x)$ $\quad [L_z, x] = i\hbar y$ $(z \to x \to y)$

③ [Angular Momentum, Linear Momentum]

$[L_x, P_x] = 0$
$[L_y, P_y] = 0$
$[L_z, P_z] = 0$

$[L_x, P_y] = i\hbar P_z$
$[L_y, P_z] = i\hbar P_x$
$[L_z, P_x] = i\hbar P_y.$
$[P_z, L_y] = -i\hbar P_x$

④ [Angular Momentum, Angular Momentum]

$[L_x, L_x] = 0$
$[L_y, L_y] = 0$
$[L_z, L_z] = 0$

$[L_x, L_y] = i\hbar L_z$
$[L_y, L_z] = i\hbar L_x$
$[L_z, L_x] = i\hbar L_y$
$[L_x, L_z] = -i\hbar L_y$

* If two operator commutes i.e. $[\hat{A}, \hat{B}] = 0$ then observable corresponding to these operator can be measured simultaneously and they will violate Heisenberg's Uncertainity Rule.

Ex:- $[K.E, P.E.] = 0$

Hence K.E. and P.E. can be calculated simultaneously.

* Ladder Operator :-

$$L_+ = L_x + iL_y$$

$$L_- = L_x - iL_y$$

Similarily;

Spin raising $S_+ = S_x + iS_y$

Spin lowering $S_- = S_x - iS_y$.

Example :-

$$[L_+, L_z] = [L_x + iL_y, L_z]$$

$$= [L_x, L_z] + i[L_y, L_z]$$

$$= -i\hbar L_y + i^2\hbar L_x$$

$$[L_+, L_z] = -\hbar[iL_y + L_x]$$

$$\boxed{[L_+, L_z] = -\hbar L_+}$$

* Note :-

$[A, B] = 0$ i.e. $AB - BA = 0 \Rightarrow \boxed{AB = BA}$

$[A, B] \neq 0$ Non-commutator.

and if $AB + BA = 0$ Anticommutator.

* Hermitian Operator :-

* Condition of Hermitian -

$\hat{A}$ = operator

ψ = wave func^n

ψ^* = complex Conjugate

$$\boxed{\int \psi^* \hat{A} \psi \, d\tau = \int \hat{\psi} \overset{*}{\hat{A}} \psi^* d\tau}$$

∵ Its very complex to evaluate above integral hence we use other conditions to check whether an operator is hermitian or not.

i.e. If,

Hermitian adjoint of operator A = Operator A

$$\boxed{(\hat{A})^\dagger = \hat{A}}$$

where,

$(\hat{A})^\dagger$ = Hermitian adjoint.

$\dagger$ (dragger) = transpose + complex conjugate = Hermitian adjoint.

* Properties of Hermitian Adjoint :-

(i) $(AB)^\dagger = B^\dagger A^\dagger$

(ii) $(A+B)^\dagger = A^\dagger + B^\dagger$

(iii) $(A-B)^\dagger = A^\dagger - B^\dagger$

(iv) $(A^n)^\dagger = (A^\dagger)^n$

(v) $(aA)^\dagger = a^* (A)^\dagger$

↳ complex conjugate of constant.

(vi) $(A^\dagger)^\dagger = A$

(vii) $\left(\frac{d}{dx}\right)^\dagger = -\frac{d}{dx}$

(viii) $(\text{Position})^\dagger = \text{Position}$

$(\hat{x})^\dagger = x$

$(\hat{y})^\dagger = y$

$(\hat{z})^\dagger = z$

*Note :- If $(A)^\dagger = A$ Hermitian

$(A)^\dagger = -A$ Non-Hermitian

$(A)^\dagger = B$ Anti Hermitian

* The sum of two Hermitian operator and difference of two Hermitian operator is also Hermitian.

Proof:- Let A and B be two hermitian operator such that;

$$(\hat{A})^\dagger = \hat{A} \quad \text{and} \quad (\hat{B})^\dagger = \hat{B}$$

$$(A \pm B)^\dagger = A^\dagger \pm B^\dagger$$
$$= A \pm B \Rightarrow (A \pm B)$$

$$\Rightarrow \boxed{(A \pm B)^\dagger = (A \pm B)}$$

* The product of two hermitian operator is not hermitian. It will be hermitian only when both the operator commute.

Let, A and B be two Hermitian operator,

$$(A^\dagger) = A \quad \text{and} \quad (B^\dagger) = B$$

Now;
$$(AB)^\dagger = B^\dagger A^\dagger$$
$$= BA$$ {hence product of two hermitian operator is not hermitian}

It will be hermitian

if, $AB = BA \Rightarrow AB - BA = 0$

$$[\hat{A}, \hat{B}] = 0$$

Hence if two hermitian operators commute with each other then their product is also hermitian otherwise it won't be hermitian.

(i) Prove that P_x is a Hermitian operator.

$$(P_x)^\dagger = \left(-i\hbar \frac{d}{dx}\right)^\dagger = (-i\hbar)^* \left(\frac{d}{dx}\right)^\dagger$$

$$= i\hbar\left(-\frac{d}{dx}\right)$$

$$= -i\hbar \frac{d}{dx} = P_x$$

$\because (P_x)^\dagger = P_x$

Hence P_x is a hermitian operator.

(ii) Prove that K_x is a Hermitian operator:

$$(K_x)^\dagger = \left(\frac{-\hbar^2}{2m}\frac{d^2}{dx^2}\right) = \left(\frac{-\hbar^2}{2m}\right)^* \left(\frac{d^2}{dx^2}\right)^\dagger$$

$$= \left(-\frac{\hbar^2}{2m}\right)\left(\left[\frac{d}{dx}\right]^\dagger\right)^2$$

$$= \left(-\frac{\hbar^2}{2m}\right)\left(\frac{-d}{dx}\right)^2$$

$$= -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}$$

$$= K_x.$$

$\because (K_x)^\dagger = K_x$

$\Rightarrow K_x$ is a hermitian operator

(iii) The commutator of two hermitian operator is anti-hermitian :-

Given, $(A)^\dagger = A$ and $(B)^\dagger = B$

$[\hat{A},\hat{B}] = ??$

But,

$$[\hat{A},\hat{B}]^\dagger = [AB - BA]^\dagger$$

$$= (AB)^\dagger - (BA)^\dagger$$

$$= B^\dagger A^\dagger - A^\dagger B^\dagger$$

$$= -\{A^\dagger B^\dagger - B^\dagger A^\dagger\}.$$

$$= -\{AB - BA\}$$

$$= -[\hat{A},\hat{B}]$$

$\because [\hat{A},\hat{B}] = -[\hat{A},\hat{B}]$

Hence commutator of two Hermitian operator is antihermitian.

* If 'i' is attached to a Hermitian operator, then it becomes antihermitian.

* If 'i' is attached to a antihermitian operator, then it becomes hermitian.

* The product of operator $\hat{A}$ and it's Hermitian adjoint is always Hermitian.

i.e. $[AA^\dagger]^\dagger = (A^\dagger)^\dagger (A)^\dagger$

$= AA^\dagger$

* We know that, If $(A)^\dagger = A$ and $(B)^\dagger = B$

$[A,B]^\dagger =$ Anti Hermitian

$i[A,B]^\dagger =$ Hermitian.

* Given operators $\hat{A}$ and $\hat{A}^\dagger$

find $(AA^\dagger)^\dagger$

$(AA^\dagger)^\dagger = (A^\dagger)^\dagger A^\dagger$

$= AA^\dagger$

find $[AA^\dagger + A^\dagger A]^\dagger$

$[AA^\dagger + A^\dagger A] = (AA^\dagger)^\dagger + (A^\dagger A)^\dagger$

$= (A^\dagger)^\dagger A^\dagger + (A^\dagger)(A^\dagger)^\dagger$

$= AA^\dagger + A^\dagger A$

} Both are Hermitian.

* Eigen Value Equation :-

$$\boxed{\hat{A}\psi = a\psi}$$

Eigen Function

Eigen Operator

Eigen Value = Value of observable.

Ex:- $\hat{A} = \frac{d}{dx}$ and $\psi = e^{ax}$

$$\hat{A}\psi = \frac{d}{dx} e^{ax}$$

$$\hat{A}\psi = a e^{ax}$$

$$\boxed{\hat{A}\psi = a\psi}$$

eigen value.

Gate $\psi = e^{ikx}$ $P_x = ?$

$$P_x\psi = -\frac{i\hbar}{\cdot}\frac{d}{dx} e^{ikx}$$

$$= (-i\hbar)(ik)e^{ikx}$$

$$= \hbar e^{ikx} \cdot k$$

$$P_x\psi = \hbar k \cdot e^{ikx}$$

$\boxed{P_x\psi = \hbar k\psi}$ hence $\boxed{P_x = \hbar k}$ for $\psi = e^{ikx}$.

Note :- If we attach a constant with any function then the eigen value ~~changes~~, do not changes.

But if we attach constant with the operator then eigen value do ~~not~~ changes

Ex :- $\psi = e^{ax}$ $\hat{A} = \frac{d}{dx}$

$$\frac{d}{dx}\psi = a e^{ax}$$

$\boxed{\text{eigen value} = a}$

$\psi = e^{ax}$ $\hat{A} = 100\frac{d}{dx}$

$$100\frac{d}{dx}\psi = 100\frac{d}{dx}e^{ax}$$

$$= 100 a e^{ax}$$

$\boxed{\text{Eigen Value} = 100a}$

$\psi = 100 e^{ax}$ $\hat{A} = \frac{d}{dx}$

$$\frac{d}{dx}\psi = 100 a e^{ax}$$

$$= a \cdot 100 e^{ax}$$

$\boxed{\text{Eigen value} = a}$

* Eigen value corresponding to Hermitian operator is always real.
* The sum of any two degenerate eigen function is also a eigen function.

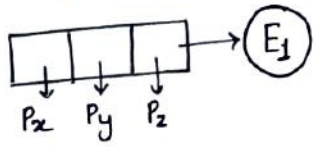
Let ψ_m and ψ_n be two eigen functions such that,

$$\boxed{\begin{aligned}\hat{A}\psi_m &= a\psi_m \\ \hat{A}\psi_n &= a\psi_n\end{aligned}}$$

Hence ψ_m and ψ_n are degenerate Eigen function.

if we operate the same operator over two different functions and they give the same eigen value then the functions are known as degenerate eigen functions.

Example :-



On Applying Hamiltonian operator.

$$\boxed{\hat{H}P_x = E_1 P_x} \quad \boxed{\hat{H}P_y = E_1 P_y} \quad \text{and} \quad \boxed{\hat{H}P_z = E_1 P_z}$$

Now,

$$\begin{aligned}\hat{A}(\psi_m + \psi_n) &= \hat{A}\psi_m + \hat{A}\psi_n \\ &= a\psi_m + a\psi_n \\ &= a(\psi_m + \psi_n)\end{aligned}$$

$$\Rightarrow \boxed{\hat{A}(\psi_m + \psi_n) = a(\psi_m + \psi_n)}$$

⇒ The sum and difference of any two degenerate eigen function is also a eigen function corresponding to the same operator.

⇒ The sum and difference of any two ~~degene~~ non-degenerate eigen function is not a eigen function corresponding to the same operator.

* Non-degenerate eigen function corresponding to Hermitian operator are orthogonal.

$$\hat{A}\psi_m = a\psi_m$$
$$\hat{A}\psi_n = b\psi_n$$

then $\boxed{\int \psi_m \cdot \psi_n \, d\tau = 0}$

∵ ∠ b/w ψ_m and $\psi_n = 90°$

and wave funcn (ψ) behaves as vector.

$$\Rightarrow \vec{\psi_m} \cdot \vec{\psi_n} = |\vec{\psi_m}||\vec{\psi_n}| \cos\theta.$$

$$\boxed{\vec{\psi_m} \cdot \vec{\psi_n} = 0}$$

* Angle b/w two wavefunctions is given by.

$$\cos\theta = \frac{\vec{\psi_m}\cdot\vec{\psi_n}}{|\psi_m||\psi_n|}$$

and

$$\boxed{\int \psi_m \cdot \psi_n \, dc = 0} \rightarrow \text{Condition of orthogonality.}$$

Example :- Calculate Kinetic Energy for particle in 1-D Box $[0-l]$ and $\psi_x = \sqrt{\frac{2}{l}} \sin\frac{n\pi x}{l}$

∵ We know that,

$$K_x = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}$$

$$K_x\psi_x = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\left(\sqrt{\frac{2}{L}}\right)\sin\frac{n\pi x}{l}.$$

$$= -\frac{\hbar^2}{2m}\frac{d}{dx}\left\{\frac{d}{dx}\left(\sqrt{\frac{2}{L}}\right)\sin\frac{n\pi x}{l}\right\}$$

$$= -\frac{\hbar^2}{2m}\sqrt{\frac{2}{L}}\left(\frac{n\pi}{l}\right)\frac{d}{dx}\cos\frac{n\pi x}{l}$$

$$= -\frac{\hbar^2}{2m}\sqrt{\frac{2}{L}}\left(\frac{n\pi}{l}\right)^2\left(-\sin\frac{n\pi x}{l}\right)$$

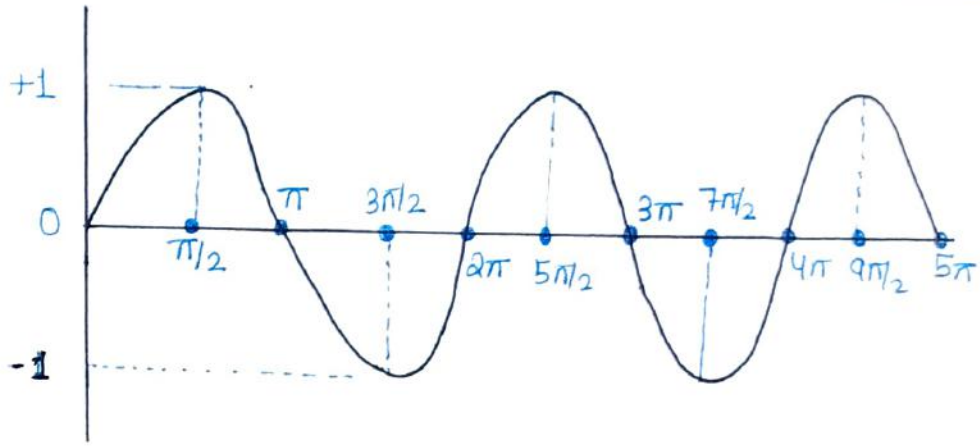
$$= \frac{\hbar^2}{2m}\sqrt{\frac{2}{L}}\left(\frac{n^2\pi^2}{l^2}\right)\sin\frac{n\pi x}{l}$$

$$= \frac{\hbar^2}{2m}\left(\frac{n^2\pi^2}{l^2}\right)\sqrt{\frac{2}{L}}\sin\frac{n\pi x}{l}$$

$$\boxed{K_x\psi = a\psi}$$

Hence, $K_x = \frac{\hbar^2}{2m}\cdot\frac{n^2\pi^2}{l^2}$

⊛ Sine Wave :-



$\sin n\pi = 0 \quad [n = 0, 1, 2, 3, 4, \ldots]$

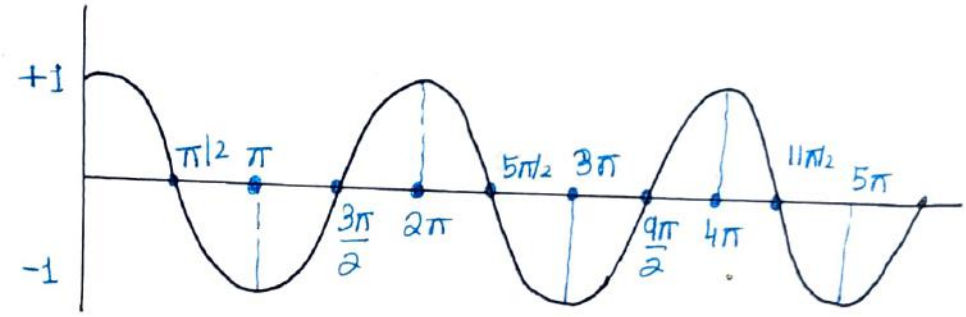
$\sin \frac{(2n+1)}{2}\pi = \pm 1$

+1 when n = even $[0, 2, 4, 6 \ldots]$

Ex:- $\sin \frac{\pi}{2}$, $\sin \frac{5\pi}{2}$, $\sin \frac{9\pi}{2}$.

-1 when n = odd $[1, 2, 3, 5, \ldots]$ Ex:- $\sin \frac{3\pi}{2}$, $\sin \frac{7\pi}{2}$, $\sin \frac{11\pi}{2}$

⊛ Cosine Wave :-



$\cos\left(\frac{2n+1}{2}\right)\pi = 0 \quad \{n = 0, 1, 2, 3 \ldots\}$

$\cos n\pi = \pm 1 \quad \{n = 0, 1, 2, 3, \ldots\}$

+1 when n = even

-1 when n = odd.

⊛ Some Important Integrations :-

① $\int \sin^2 bx \, dx = \frac{x}{2} - \frac{1}{4b} \sin 2dx.$

② $\int \cos^2 bx \, dx =$

⊛ Probability And Normalisation :-

According to Einstein, Intensity is directly proportional to square of amplitude. i.e,

$$I \propto (A)^2$$

Similarily, Probable density $\propto |\psi|^2$; ψ = wave func^n.

$$P.D. = \frac{P}{\text{Volume Element}}.$$

$$\boxed{\text{Probability} = \text{Probable density} \times \text{Volume Element.}}$$

$$\boxed{P = \psi^2 \, d\tau}$$

$$\boxed{P = \int_a^b \psi^* \psi \, d\tau}$$

If $\psi = A + iB$

$\psi^* = A - iB$

For 1-D Box :- $d\tau = dx$

For 2-D Box :- $d\tau = dx\,dy$

For 3-D Box :- $d\tau = dx\,dy\,dz$

For H-atom :- $d\tau = r^2 dr \sin\theta \, d\theta \, d\phi$. = TIFR

For 1-D Box with limit $[0-l]$, wave function is given by,

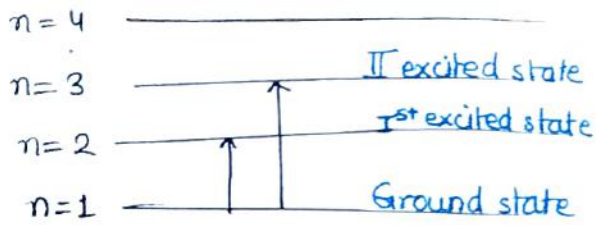
$$\boxed{\psi_n = \sqrt{\frac{2}{l}} \sin \frac{n\pi x}{l}}$$

n = Translational Quantum Number.

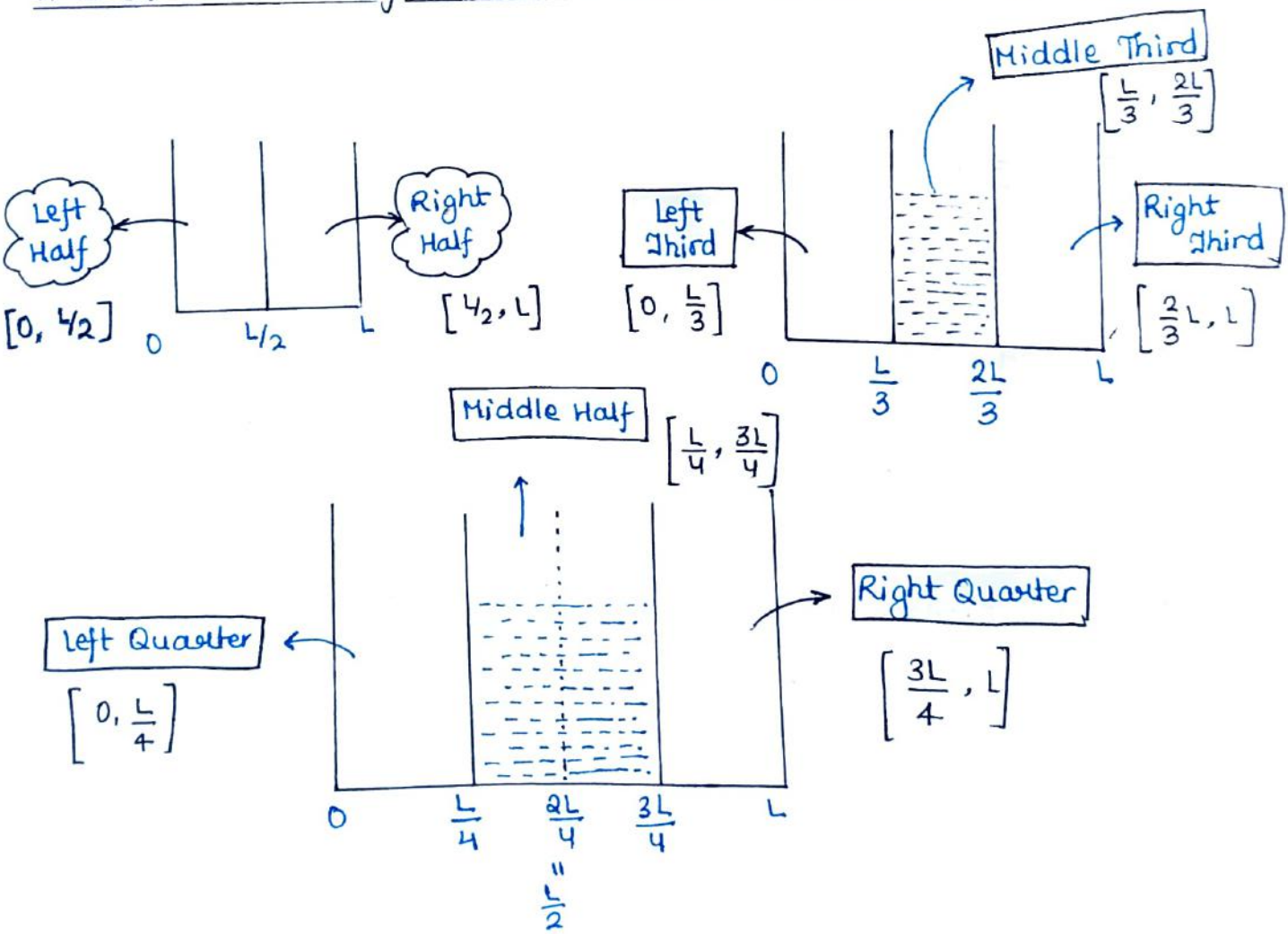
$\psi_1 = \sqrt{\frac{2}{L}} \sin \frac{\pi x}{l}$ $n=1$

$\psi_2 = \sqrt{\frac{2}{L}} \sin \frac{2\pi x}{l}$ $n=2$

$\psi_3 = \sqrt{\frac{2}{L}} \sin \frac{3\pi x}{l}$ $n=3$



* Distribution of 1-D Box into Various Limits :- $\{0, L\}$



⊛ Calculation of Probability for 1-D Box having limit $[0, l]$

We know that for 1-D Box $[0, l]$

$$\psi = \sqrt{\frac{2}{l}} \sin \frac{n\pi x}{l}$$

$n = 1, 2, 3, \ldots\ldots$

$$\psi^* = \sqrt{\frac{2}{l}} \sin \frac{n\pi x}{l}$$

1D-box ; $d\tau = dx$

$$P = \int_a^b \psi^* \psi \, d\tau = \int_a^b \sqrt{\frac{2}{l}} \sin \frac{n\pi x}{l} \cdot \sqrt{\frac{2}{l}} \sin \frac{n\pi x}{l} \, dx$$

$$\boxed{\because \int \sin^2 bx \, dx = \frac{x}{2} - \frac{1}{4b} \sin 2bx}$$

$$P = \frac{2}{l} \int_a^b \sin^2 \frac{n\pi x}{l} \, dx$$

$$\boxed{P = \frac{2}{l} \left[\frac{x}{2} - \frac{l}{4n\pi} \sin \frac{2n\pi x}{l} \right]_a^b}$$

or

It can be written as,

$$\boxed{P = \left[\frac{x}{l} - \frac{1}{2n\pi} \sin \frac{2n\pi x}{l} \right]_a^b}$$

General expression to calculate probability for 1-D box with limit $[0, l]$.

⊛ Normalisation:-

Condition of Normalisation,

$$\boxed{\int \psi^* \psi \, d\tau = 1}$$

Difference b/w probability and Normalisation.

$$\boxed{P = \int_a^b \psi^* \psi \, d\tau}$$

and if ψ is a normalised wave function, then probability of finding the particle is 100% i.e. 1.

$$\int_{\text{entire space/entire limit}} \psi^* \psi = 1$$

⁕ How to normalise a given func^n (ψ) if,

$$\int \psi^* \psi \neq 1 \quad \text{and} \quad \int \psi^* \psi = N.$$

If on applying condition of Normalisation we get a value say 'N' other than '1' then the given func^n 'ψ' is not normalised. In such cases:

1.) Find the reciprocal of 'N' $\underset{\text{its root}}{\cancel{N}} = \sqrt{\frac{1}{N}}$ (known as Normalisation Constant) N.C.

2.) Attach this N.C. to the given function ψ.

3.) Our new wave func^n is normalised.

Ex: $\int \psi^* \psi \, d\tau = N.$

$$\Rightarrow \quad N.C = \sqrt{\frac{1}{N}}$$

New wave func^n $= \sqrt{\frac{1}{N}} \psi$

Hence $\psi = \sqrt{\frac{1}{N}} \psi$ is our new normalised wave function.

Ex:- Check whether $\psi(x) = x$ is normalised or not.

$\psi = x$ in $[0,1]$

For a wave function to be normalised we have,

$$\int \psi^* \psi \, d\tau = 1$$

$$= \int_0^1 x \cdot x \, dx = \int_0^1 x^2 \, dx = \left[\frac{x^3}{3}\right]_0^1 = \frac{1}{3}.$$

$\because$ Given wave function is not normalised.

$$NC = \sqrt{\frac{1}{N}} = \sqrt{3}$$

$$\boxed{\psi_{new} = \sqrt{3}x}$$

Above wave function is our normalised wave function.

Ex:- Check whether $\psi = \sin\frac{\pi x}{l}$ in $[0, l]$ is normalised or not.

$$\int \psi^* \psi = \int_0^l \sin\frac{\pi x}{l} \times \sin\frac{\pi x}{l} \, dx$$

$$= \int_0^l \sin^2\frac{\pi x}{l} \, dx$$

$$= \left[\frac{x}{2} - \frac{l}{4\pi}\sin\frac{2\pi x}{l}\right]_0^l = \left[\frac{x}{2} - \frac{l}{4\pi}\sin\frac{2\pi x}{l}\right]_0^l$$

$$= \left[\frac{l}{2} - \frac{l}{4\pi}\right] = \left[\frac{x}{2} - \frac{l}{4\pi}\sin\frac{2\pi x}{l}\right]_0^l$$

$$= \left[\frac{l}{2} - \frac{l}{4\pi}\sin\frac{2\pi l}{l}\right] - \left[0 - \frac{l}{4\pi}\sin\frac{2\pi 0}{l}\right]$$

$$\int \psi^* \psi \, dx = \frac{l}{2}$$

$$\because \int \psi^* \psi \, dx \neq 1.$$

$$N.C. = \sqrt{\frac{2}{l}}$$

$\boxed{\psi = \sqrt{\frac{2}{l}}\sin\frac{\pi x}{l}}$ is our normalised wave function.

* Average Value Method / Expectation Value:-

In Quantum mechanics there are two ways to calculate the value of observable :

(i) Eigen Value Equation :- If the operator and the function follows eigen value eq^n then we can easily find the value of observable. i.e.

$$\boxed{\hat{A}\psi = a\psi}$$

a → value of observable.

Ex:- $\psi_n = \sqrt{\frac{2}{l}} \sin \frac{n\pi x}{l}$

$\hat{A} = K.E.$

$$K.E.\,\psi = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\sqrt{\frac{2}{l}}\sin\frac{n\pi x}{l}$$

$$= \frac{n^2\hbar^2\pi}{2ml^2}\sqrt{\frac{2}{l}}\sin n\pi x$$

$$\boxed{K.E. = \frac{n^2\hbar^2\pi}{2ml^2}}$$

But it is not necessary that every operator in quantum mechanics follow eigen value equation with a given func^n.

Ex:- $\psi_n = \sqrt{\frac{2}{l}} \sin \frac{n\pi x}{l}$ $\quad \hat{A} = P_x$

$$P_x\psi = -i\hbar\frac{d}{dx}\sqrt{\frac{2}{l}}\sin\frac{n\pi x}{l}$$

$$= \left[(-i\hbar)\sqrt{\frac{2}{l}}\frac{n\pi}{l}\right]\cos\frac{n\pi x}{l}$$

Hence momentum operator does not follow eigen value equation with the func^n ψ.

→ Hence for such cases we use expectation value method.

Expectation Value :-

$$\boxed{\underset{\text{observable}}{\langle M\rangle} = \frac{\int \psi^* M \psi \, d\tau}{\int \psi^* \psi \, d\tau}}$$

If function is normalised, $\int \psi^*\psi \, d\tau = 1$

$$\boxed{\langle M\rangle = \int \psi^* M \psi \, d\tau}$$

Note:- The value of observable calculated by the eigen value method and expectation value method are same.

Ex:- Calculate average value for the function $\psi = (x)$ and $\hat{A} = \hat{x}$. in $[0,1]$

We know that $(\hat{x})$ is a position operator.

$$\langle x \rangle = \frac{\int_0^1 \psi^* x \psi \, d\tau}{\int \psi^* \psi \, d\tau}$$

$$= \frac{\int_0^1 x \cdot x \cdot x \, dx}{\int_0^1 x \cdot x \, dx}$$

$$\langle x \rangle = \frac{\int_0^1 x^3 dx}{\int_0^1 x^2 dx} = \frac{\left[\frac{x^4}{4}\right]_0^1}{\left[\frac{x^3}{3}\right]_0^1} = \frac{\left[\frac{1}{4} - 0\right]}{\left[\frac{1}{3} - 0\right]}$$

$$\boxed{\langle x \rangle = \frac{3}{4}}$$

⊛ Schrodinger Wave Equation :-

Schrodinger wave equation is the Eigen value equation of Energy.

We know that for Energy being observable we use Hamiltonian operator in quantum mechanics.

$$\boxed{\hat{H}\psi = E\psi}$$

$\hat{H}$ → Hamiltonian Operator

E → Energy.

and we know that,

$$\hat{H} = P.E. + K.E.$$

$$\hat{H} = \frac{-\hbar^2}{2m}\nabla^2 + V$$

where $\boxed{\nabla^2 = \frac{d^2}{dx^2} + \frac{d^2}{dy^2} + \frac{d^2}{dz^2}}$

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + V\right)\psi = E\psi$$

$$\boxed{-\frac{\hbar^2}{2m}\nabla^2\psi + V\psi = E\psi} \quad \text{—— (i)}$$

Multiply eq^n-1 by $-\frac{2m}{\hbar^2}$.

$$\nabla^2\psi - \frac{2m}{\hbar^2}V\psi = -\frac{2m}{\hbar^2}E\psi$$

$$\nabla^2\psi + \frac{2m}{\hbar^2}\left[E\psi - V\psi\right] = 0$$

$$\boxed{\nabla^2\psi + \frac{2m}{\hbar^2}(E-V)\psi = 0} \quad \text{—— (ii)}$$

Equation-(ii) is the required Schrodinger Wave equation.

$$\boxed{\nabla^2\psi + \frac{8\pi^2 m}{h}(E-V)\psi = 0} \quad \text{modified form } \left\{\hbar = \frac{h}{2\pi}\right\}$$

Hence Schrodinger Wave equa^n is an eigen value equation where operator is hamiltonian and eigen value is Energy.

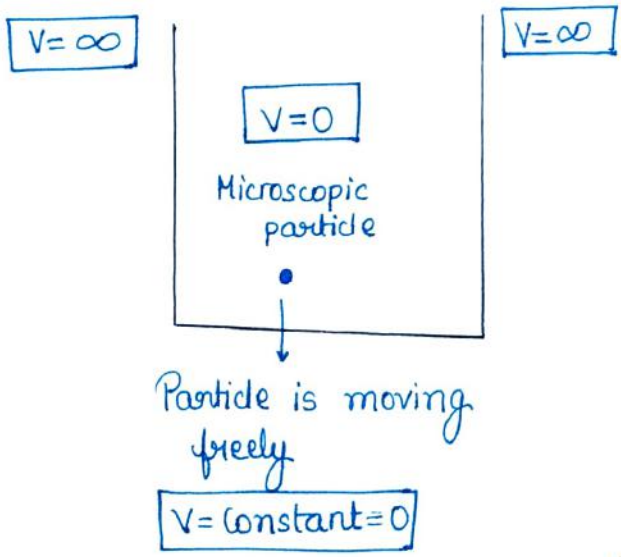
⊛ Application Of Schrodinger Wave Equation :-

1) Translational Motion ⇒ PIB Model
2) Electronic Motion ⇒ Hydrogen Atom.
3) Vibrational Motion ⇒ SHO
4) Rotational Motion ⇒ Rigid Rotor.

(I) PIB Model :- It is studied under translational Motion.

Three parts are studied in it.

- 2-D Box
- 1D-Box
- 3-D Box.



Microscopic particle shows tunneling effect, given by,

$$\boxed{T = e^{-2\beta L}} \quad \text{where} \quad \boxed{\beta = \frac{\sqrt{2M(V-E)}}{\hbar}}$$

$$\boxed{T = e^{-2\frac{\sqrt{2M(V-E)}}{\hbar}\cdot L}}$$

when $V=\infty$

$$T = e^{-\infty} = 0$$

Hence at infinite potential Microscopic particle can not show tunneling effect.

<u>Applying Schrodinger Wave Equation to find wave function for the particle in 1-D Box. [0, L]</u>

for 1D Box; $\nabla^2 = \frac{d^2}{dx^2}$.

Applying Schrodinger Wave Equation,

$$\nabla^2\psi + \frac{2m}{\hbar^2}(E-V)\psi = 0$$

<u>For 1-D Box</u>:-

$$\frac{d^2\psi}{dx^2} + \frac{2mE}{\hbar^2}[E-0]\psi = 0 \qquad \because V_{inside} = 0$$

$$\frac{d^2\psi}{dx^2} + \frac{2mE}{\hbar^2}\psi = 0$$

Let, $\boxed{\frac{2mE}{\hbar^2} = k^2}$

$$\boxed{\frac{d^2\psi}{dx^2} + k^2\psi = 0} \quad \text{—(i)}$$

On solving (i) we get,

$\boxed{\psi = A\sin kx + B\cos kx}$ → using this wave func^n and neglecting other we have,

$$\psi = Ae^{ikx} + Be^{-ikx}$$

$$\psi = A\sin Kx + B\cos kx \quad \text{——} (*)$$

Applying Boundary Conditions:-

(i) $x=0 \quad \psi=0$

$$0 = A\sin 0^\circ + B\cos 0^\circ$$

$$0 = B\cos 0^\circ \qquad [\because \cos 0^\circ = 1]$$

$$\Rightarrow \boxed{B=0}$$

Putting in $*$ we have,

$$\boxed{\psi = A\sin Kx} \text{——} \{*^2\}$$

(ii) $x=l \quad \psi=0$

$$0 = A\sin kl$$

$$\because A \neq 0 \Rightarrow \sin kl = 0$$

$$\sin kl = \sin n\pi$$

$$\boxed{k = \frac{n\pi}{l}}$$

Hence our wave function comes out as,

$$\boxed{\psi = A\sin \frac{n\pi}{l}x}$$

here, $n = 1, 2, 3, 4, \ldots\ldots$

$\downarrow$

Translational Quantum Number.

Value of n can never be zero otherwise func^n will vanish.

$\because$ Our wave func^n $\psi = A\sin\frac{n\pi x}{l}$ is not normalised. Therefore by using condition of normalisation we will normalise the given wave function.

$$\psi = A\sin\frac{n\pi x}{l}.$$

$$\boxed{\int \psi^* \psi \, d\tau = 1} \rightarrow \text{Condition of Normalisation.}$$

$$= \int_0^l A\sin\frac{n\pi x}{l} . A\sin\frac{n\pi x}{l} \, dx = 1$$

$$= A^2 \int_0^l \sin^2\frac{n\pi x}{l} \, dx = 1$$

$$= A^2 \left[\frac{x}{2} - \frac{l}{4n\pi}\sin\frac{2n\pi x}{l}\right]_0^l = 1$$

On applying limit we have,

$$A^2\left[\frac{l}{2} - \frac{l}{4n\pi}\sin\frac{n\pi l}{l}\right] - A^2[0] = 1$$

$$A^2 \cdot \frac{l}{2} = 1$$

$$\boxed{A = \sqrt{\frac{2}{l}}}$$

Hence our normalised wave function is,

$$\boxed{\psi = \sqrt{\frac{2}{L}}\sin\frac{n\pi x}{l}}$$

Now, we have assumed,

$$K^2 = \frac{2mE}{\hbar^2} \quad \text{—(i)}$$

and

$$K = \frac{n\pi}{l} \quad \text{—(ii)}$$

Equating (i) and (ii) we have,

$$\frac{n^2\pi^2}{l^2} = \frac{2mE}{\hbar^2}$$

$$E = \frac{\hbar^2}{2m}\cdot\frac{n^2\pi^2}{l^2}$$

$$\boxed{E = \frac{n^2\pi^2\hbar^2}{2ml^2}}$$

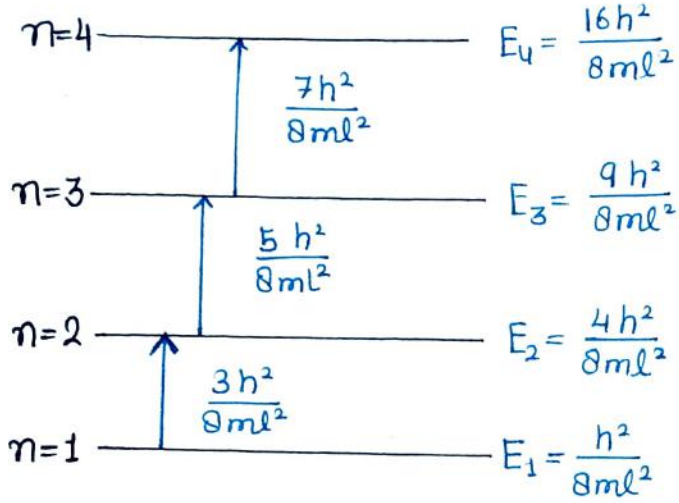
This is the expression for total energy and the result is same as that of K.E. operator over the same func^n

$\Rightarrow$ $\boxed{\text{Kinetic Energy of Particle in 1-D Box} = \text{Total Energy of the particle}}$

Now; $E_n = \dfrac{n^2\pi\hbar^2}{2ml^2}$

$\because \left[\hbar = \dfrac{h}{2\pi}\right]$

$$\boxed{E_n = \frac{n^2h^2}{8ml^2}}$$



Hence in 1-D Box, the energy spacing ↑ses as the value of Translational Quantum Number increases.

* Plot of Ψ and Ψ^2:-

For ground state, $n=1$

$$\psi_1 = \sqrt{\frac{2}{l}} \sin \frac{\pi x}{l}$$

Compairing we have,

$$\frac{\pi x}{l} = \frac{\pi}{2}$$

$\boxed{x = l/2}$, Hence we will have maxima at $x = \frac{l}{2}$.

when,

$$\frac{\pi x}{l} = \frac{5\pi}{2}$$

$\boxed{x = 2.5l}$ This is not possible at value of 'x' exceeds boundary condition.

~~Hence bour~~

Hence there will be only one maxima at ground state.

For maximum value,

$$\boxed{\sin \frac{\pi x}{l} = 1}$$

possible only when,

$$\frac{\pi x}{l} = \frac{\pi}{2}, \frac{5\pi}{2}, \frac{9\pi}{2}.$$

* For minimum value;

$$\sin \frac{\pi x}{l} = -1$$

possible only when, $\frac{\pi x}{l} = \frac{3\pi}{2}, \frac{7\pi}{2}, \frac{11\pi}{2}, \ldots$

$\frac{\pi x}{l} = \frac{3\pi}{2} \Rightarrow$ $\boxed{x = 1.5l}$ It also exceeds boundary cond^n hence, minima not possible in ground state

Node :- Value or points on the graph where wave function vanishes, except boundary points.

i.e. $\boxed{\psi = 0}$ $\boxed{\sin\frac{\pi x}{l} = 0}$

possible only when $\frac{\pi x}{l} = 0, \pi, 2\pi, 3\pi, 4\pi, \ldots\ldots$

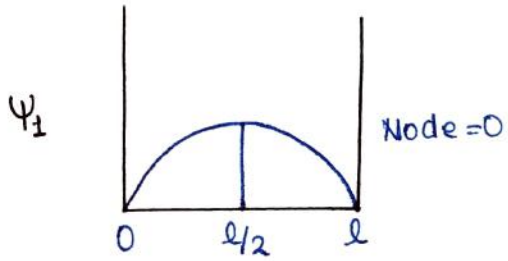
when, $\frac{\pi x}{l} = 0$ $\frac{\pi x}{l} = \pi$

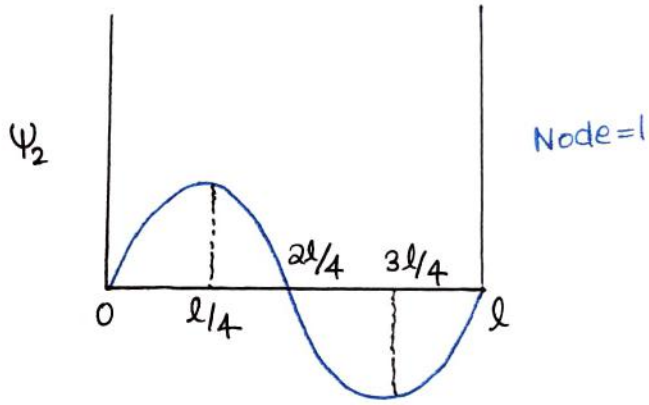
$\boxed{x = 0}$ $\boxed{x = l}$

Both are boundary condition.

Hence no node is present in ground state.

* Graph for Ground State :-





Trick to Remember

Order of Graph-Polation; Maxima → Node → Minima → Node → Maxima → Node → Minima

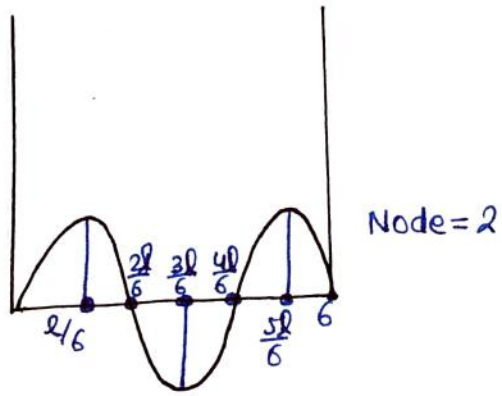
Value of maxima and nodes, $= \frac{l}{2n}$.

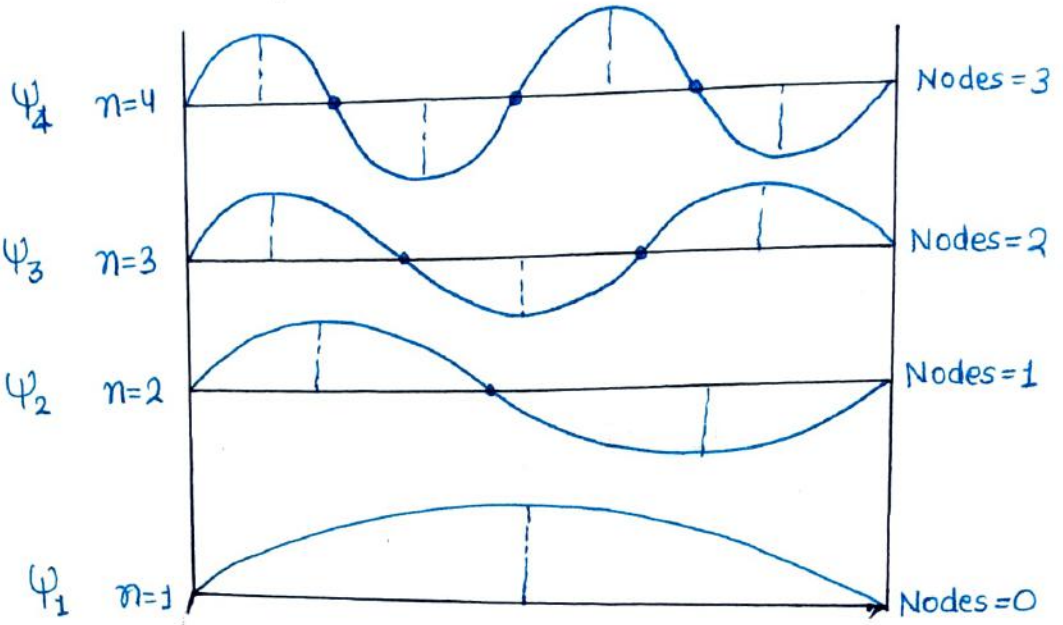
Ex for ψ_2, $n=2$

Maxima $= \frac{l}{4}$ Node $= \frac{l}{4} + \frac{l}{4} = \frac{2l}{4}$ Minima $= \frac{2l}{4} + \frac{l}{4} = \frac{3l}{4}$ Node $= \frac{3l}{4} + \frac{l}{4} = l$ boundary.

Ex: for ψ_3, $n=3$

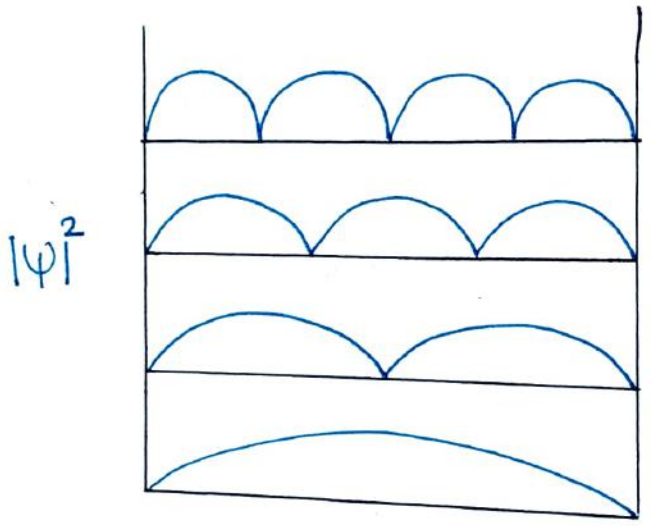
Maxima $= \frac{l}{6}$ Node $= \frac{2l}{6}$ Minima $= \frac{3l}{6}$ Node $= \frac{4l}{6}$ Maxima $= \frac{5l}{6}$ Boundary $= l$.





and odd ψ → symmetric $\{\psi_1, \psi_3, \psi_5, \psi_7\}$

even ψ → antisymmetric $\{\psi_2, \psi_4, \psi_6\}$



* Calculation of length of the box :-

We know that,

$$E = \frac{n^2h^2}{8ml^2} \longrightarrow (K.E) \text{ (i)}$$

and

$$K.E. = \frac{P^2}{2m} \quad \text{and} \quad P = \frac{h}{\lambda}$$

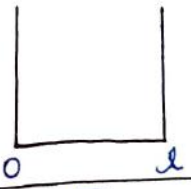
$$\boxed{K.E. = \frac{h^2}{2m\lambda^2}} \text{ —— (ii)}$$

Equating (i) and (ii)

$$\frac{n^2h^2}{8ml^2} = \frac{h^2}{2m\lambda^2} \Rightarrow \boxed{l = \frac{n\lambda}{2}}$$

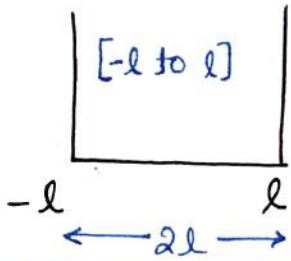
Hence length of the box is half of the wavelength or integral multiple of half of the wavelength.

* Variation in limits of 1-D Box :-



$$\boxed{\psi_n = \sqrt{\frac{2}{l}} \sin \frac{n\pi x}{l}}$$

$$\boxed{E_n = \frac{n^2 h^2}{8ml^2}}$$



Hence 'l' will be replaced by '2l'

ψ_n — n=even (2, 4, 6, 8...) →

$$\psi_n = \sqrt{\frac{2}{2l}} \sin \frac{n\pi x}{2l}$$

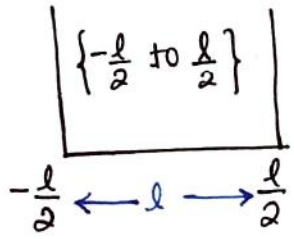
$$\boxed{\psi_n = \sqrt{\frac{1}{l}} \sin \frac{n\pi x}{2l}}$$

ψ_n — n=odd (1, 3, 5, 7...) →

$$\psi_n = \sqrt{\frac{2}{2l}} \cos \frac{n\pi x}{2l}$$

$$\boxed{\psi_n = \sqrt{\frac{1}{l}} \cos \frac{n\pi x}{2l}}$$

$$E_n = \frac{n^2 h^2}{8m(2l)^2} \Rightarrow \boxed{E = \frac{n^2 h^2}{32\, ml^2}}$$



ψ_n — n=even →

$$\boxed{\psi_n = \sqrt{\frac{2}{l}} \sin \frac{n\pi x}{l}}$$

ψ_n — n=odd →

$$\boxed{\psi_n = \sqrt{\frac{2}{l}} \cos \frac{n\pi x}{l}}$$

$$\boxed{E_n = \frac{n^2 h^2}{8ml^2}}$$

Note :- Functions are multiplicative in nature and energy is additive in nature.

⊛ 2-D Box :- There can be two types of 2-D Box.

1.) Rectangular Box

$0 < x < a$
and $0 < y < b$ {Variations along x & y axis}

$\because$ Functions are multiplicative in nature and energy is additive in nature.

$$\psi_{n_x n_y} = \psi_{n_x} \cdot \psi_{n_y}$$

$$\boxed{\psi_{n_x n_y} = \sqrt{\frac{2}{a}} \sin \frac{n_x \pi x}{a} \cdot \sqrt{\frac{2}{b}} \sin \frac{n_y \pi y}{b}}$$

$$E_{n_x n_y} = E_{n_x} + E_{n_y}$$

$$\boxed{E_{n_x n_y} = \frac{n_x^2 h^2}{8ma^2} + \frac{n_y^2 h^2}{8mb^2}}$$

2.) Square Box

$0 < x < a$
$0 < y < a$ $\{\because a = b\}$

$$\psi_{n_x n_y} = \psi_{n_x} \cdot \psi_{n_y}$$

$$\boxed{\psi_{n_x n_y} = \sqrt{\frac{2}{a}} \sin \frac{n_x \pi x}{a} \cdot \sqrt{\frac{2}{a}} \sin \frac{n_y \pi y}{a}}$$

$$E_{n_x n_y} = E_{n_x} + E_{n_y}$$

$$\boxed{E_{n_x n_y} = \frac{n_x^2 h^2}{8ma^2} + \frac{n_y^2 h^2}{8ma^2}}$$

⊛ n_x and n_y are two quantum numbers.

⊛ Concept of degeneracy will be involved in 2-D square box.

Degeneracy :- Availibity or presence of more than one state at one energy level is known as degeneracy.

Quantum Numbers :- When restrictions are imposed on a number during the solution of schrodinger wave equations the numbers are known as quantum numbers.

In Quantum, Value of quantum number can not be zero.

* Degeneracy in 2-D Box :- {Square}

$$E_{n_x n_y} = \frac{h^2}{8ma^2}[n_x^2 + n_y^2] = \frac{h^2 \pi^2}{2ma^2}[n_x^2 + n_y^2]$$

(1,3) (3,1) ψ_{13} and ψ_{31} ; $E = \frac{10h^2}{8ma^2}$; $g = 2$

(2,2) (n_x n_y) ψ_{22} ; $E = \frac{8h^2}{8ml^2}$; $g = 1$

(1,2) (n_x n_y) (2,1) (n_x n_y) ψ_{12} and ψ_{21} {wavefunc^{n}s} ; $E = \frac{5h^2}{8ma^2}$ $\because$ 2 states at same energy level = degeneracy.

(1,1) (n_x n_y) ψ_{11} and $E = \frac{2h^2}{8ma^2}$; $g = 1$

Hence, $\boxed{g = 2}$

* Trick to solve degeneracy :-

Examples :- $E_{2D} = \frac{10\,h^2}{8ma^2}$

∵ We know that,

$$E = \frac{h^2}{8ma^2}[n_x^2 + n_y^2]$$

$$\Rightarrow \frac{h^2}{8ma^2}[n_x^2 + n_y^2] = \frac{10\,h^2}{8ma^2}$$

$$\Rightarrow \boxed{n_x^2 + n_y^2 = 10}$$

Only two combinations n_x and n_y are possible for above equation.

$n_x = 1 \quad n_y = 3$ and $n_x = 3 \quad n_y = 1$

i.e. (1, 3) and (3, 1) , Hence degeneracy = $\boxed{g = 2}$

Example :- $E_{2D} = \frac{25\,h^2}{8ma^2}$. Again on compairing we have,

$$\boxed{n_x^2 + n_y^2 = 25}$$

Possible Combination :- (4, 3) and (3, 4) Hence degeneracy = $g = 2$.

Example :- $E_{2D} = \frac{50\,\hbar^2\pi^2}{2ma^2}$

On compairing with , $E = \frac{\hbar^2\pi^2}{2ma^2}[n_x^2 + n_y^2]$

$$\Rightarrow \boxed{n_x^2 + n_y^2 = 50}$$

Possible Combinations :- (7, 1) and (1, 7) and (5, 5) Hence degeneracy = $g = 3$

↳ Value of quantum numbers are entirely different hence called accidental degeneracy.

* 3-D Box :-

We will consider cubic box only. $\left\{ \begin{array}{l} 0<x<a \\ 0<y<a \\ 0<z<a \end{array} \right\}$

Wave function = $\psi_{(n_x, n_y, n_z)} = \psi_{n_x} \cdot \psi_{n_y} \cdot \psi_{n_z}$

$$\boxed{\psi_{n_x,n_y,n_z} = \sqrt{\frac{2}{a}} \sin \frac{n_x \pi x}{a} \sqrt{\frac{2}{a}} \sin \frac{n_y \pi y}{a} \sqrt{\frac{2}{a}} \sin \frac{n_z \pi z}{a}}$$

Energy, $\boxed{E = E_{n_x} + E_{n_y} + E_{n_z}}$

$$E = \frac{n_x^2 h^2}{8ma^2} + \frac{n_y^2 h^2}{8ma^2} + \frac{n_z^2 h^2}{8ma^2}$$

$$\boxed{E_{3D} = \frac{h^2}{8ma^2}\left(n_x^2 + n_y^2 + n_z^2\right)}$$

$$\boxed{E_{3D} = \frac{h^2}{8ma^2}\left(n_x^2 + n_y^2 + n_z^2\right) = \frac{\hbar^2 \pi^2}{2ma^2}\left(n_x^2 + n_y^2 + n_z^2\right)}$$

* Concept of Degeneracy :-

	(2,2,2)		ψ_{222} and $E = \frac{12h^2}{8ma^2}$; $g=1$
(3,1,1)	(1,3,1)	(1,1,3)	$\psi_{311}, \psi_{131}, \psi_{113}$ and $E = \frac{11h^2}{8ma^2}$; $g=3$
(2,2,1)	(2,1,2)	(1,2,2)	$\psi_{221}, \psi_{212}, \psi_{122}$ and $E = \frac{9h^2}{8ma^2}$; $g=3$
(1,2,1)	(1,1,2)	(2,1,1)	$\psi_{121}, \psi_{112}, \psi_{211}$ and $E = \frac{6h^2}{8ma^2}$; $g=3$
	(1,1,1)		ψ_{111} and $E = \frac{3h^2}{8ma^2}$; $g=1$

*** Exampe** $E_{3D} = \frac{9h^2}{8ma^2}$ On compairing with $E_n = \frac{h^2}{8ma^2}\left[n_x^2 + n_y^2 + n_z^2\right]$

we have; $n_x^2 + n_y^2 + n_z^2 = 9$

Possible Combinations = (2, 2, 1) (2, 1, 2) (1, 2, 2) Hence $g=3$.

Example : $E_{3D} = \frac{27\hbar^2\pi^2}{2ma^2}$; On compairing we get,

$n_x^2 + n_y^2 + n_z^2 = 27$

Possible Combinations = (5, 1, 1) (1, 1, 5) $\underbrace{(1, 5, 1) \text{ and } (3, 3, 3)}_{\text{accidental degeneracy}}$.

HYDROGEN ATOM

* Some Important terms :-

Volume Element ($d\tau$) → For 1-D Box = dx

For 2-D Box = $dx\,dy$

For 3-D Box = $dx\,dy\,dz$

For Hydrogen Atom = $r^2 dr \sin\theta\, d\theta\, d\phi$.

Cartesian Co-ordinates = $[x, y, z]$

Polar Co-ordinates = $[r, \theta, \phi]$

r → $[0-\infty]$, θ → $[0-\pi]$, ϕ → $[0-2\pi]$

Lapalacian operator $\nabla^2 = \frac{d^2}{dx^2} + \frac{d^2}{dy^2} + \frac{d^2}{dz^2}$.

For H-atom ; $$\boxed{\nabla^2 = \frac{1}{r^2}\frac{d}{dr} r^2 \frac{d}{dr} + \frac{1}{r^2 \sin\theta}\frac{d}{d\theta}\sin\theta\frac{d}{d\theta} + \frac{1}{r^2 \sin^2\theta}\frac{d^2}{d\phi^2}}$$

→ H-atom model was proposed for Hydrogenic species i.e. Li^{++}, He^{+}, Be^{3+} and so on i.e. single $e^{\ominus}$ system.

→ It is studied under electronic motion.

* In case of PIB model, potential energy inside the box is zero but in case of Hydrogen atom it is not so. i.e. potential energy is not zero.

* The solution of schrodinger wave equation gives wave func^n for H-atom which consists of two different parts → Radial Part, Angular Post.

Wave function for H-atom,

$$\boxed{\psi_{(r,\theta,\phi)} = R(r)\,Y(\theta,\phi)}$$

Three different parts → Three quantum numbers, $\psi(n, l, m)$

Radial Part → depends upon two quantum numbers $R(n, l)$

Angular Part → depends upon two quantum numbers $Y(l, m)$

$n = 1, 2, 3, 4, \ldots\ldots$
$l = 0, 1, 2, 3, \ldots\ldots$
$m = 0, \pm1, \pm2, \pm3 \ldots\ldots$

⊛ Identification Of Radial Part :-

General Expression for Radial Part is given by.

$$\boxed{R_{(n,l)} = \left(\frac{2Zr}{na}\right)^{l} e^{-\frac{Zr}{na_0}}}$$

→ gives value of quantum number (n).

a_0 = Bohr radius.

→ gives value of quantum number (l).

Example :-

$$\psi = N e^{-\frac{r}{a_0}}$$

There is no free 'r' term,

i.e. $r^0 \Rightarrow \boxed{l=0}$ ⇒ 1s orbital

and $\frac{r}{a_0} = \frac{r}{na_0} \Rightarrow \boxed{n=1}$

Hence given wave function is for 1s-orbital.

Example :- $\psi = r e^{-\frac{r}{2a_0}}$

We have free 'r', On compairing we get,

$r^1 = r^l$ and $\frac{r}{2a_0} = \frac{r}{na_0}$

$\Rightarrow \boxed{l=1}$ $\Rightarrow \boxed{n=2}$

→ 2p orbital.

Example :- $\psi = N(r^2 - 2r + 1)\, e^{-\frac{r}{3a_0}}$

In above wave func^n we will not consider 'r' in given polynomial.

For the value of 'l' we require free 'r'.

Hence again we have,

$r^0 = r^l \Rightarrow \boxed{l=0}$

and $\frac{r}{3a_0} = \frac{r}{na_0} \Rightarrow \boxed{n=3}$

→ 3s orbital

Example :- $\psi = N\left[2 - \frac{r}{a^0}\right] e^{-\frac{r}{2a_0}}$

Again we do not have any free (r) hence

$l=0$, $n=2$ → 2s orbital.

⊛ Identification of Angular Part :

General Expression For Angular Part is given by;

$$\boxed{Y_{(m,l)}(\theta,\phi) = \sin^{|m|}\theta \cos^{l-|m|}\theta \, e^{im\phi}}$$

→ Gives value of (m)

→ Gives value of (l).

Example :-

$$Y(\theta,\phi) = N\cos\theta$$

On compairing we get, $e^{im\phi} = e^{0}$

$\Rightarrow \boxed{m=0}$

and, $\cos\theta = \cos^{l-|m|}\theta$

$\Rightarrow l-|m|=1$

$\boxed{l=1}$

Hence $l=1$, $m=0$.

Example :-

$$Y(\theta,\phi) = N\sin\theta\cos\theta\, e^{-i\phi}$$

On compairing we get,

$e^{-i\phi} = e^{im\phi}$

$\Rightarrow \boxed{m=-1}$

and $\cos\theta = \cos^{l-|m|}\theta$

$\Rightarrow$ ~~$l-|m|=0$~~

$\Rightarrow l-|m|=1 \Rightarrow l-|-1|=1$

$|-1|=1$

$l-1=1$

$\boxed{l=2}$

Hence $\boxed{m=-1}$ $\boxed{l=2}$

⊛ Radial Nodes and Angular Nodes :-

$\boxed{\text{Radial Nodes} = n-l-1}$

$\boxed{\text{Angular Nodes} = l}$

$\boxed{\text{Total Nodes} = n-1}$

For 1s orbital :-

$\boxed{1s}$ $n=1$, $l=0$

Radial Node = 0

$\boxed{2s}$ $n=2$, $l=0$ Radial Node = 1.

Example :- $\psi = N e^{-r/a_0}$

There are two ways to calculate the radial node for the above wave functions.

(I) Equate the radial part $=0$ and find the value of r.

No. of values of 'r' give no. of nodes present and value of 'r' gives the position of node.

$$\Rightarrow \boxed{e^{-r/a_0} = 0} \text{ —(i)}$$

equation (i) will be zero only if $r = \infty$ as $e^{-\infty} = 0$

$$\Rightarrow r = \infty \qquad \text{but } r \to [0, \infty]$$

Hence this is boundary condition and nodes are not present at boundary.

(II) Compare the equa^n with general eq^n and find values of n and l.

→ On compairing we get that there is no free 'r'.

$$\Rightarrow \boxed{l=0} \text{ and } \frac{r}{a_0} = \frac{r}{na_0} \Rightarrow \boxed{n=1}$$

Radial Nodes $= n - l - 1$

$= 1 - 0 - 1 = 0.$

Hence we get to know that no radial nodes are present for the above wave function.

Example :- $\psi = N\left(2 - \frac{r}{a_0}\right) e^{-\frac{r}{2a_0}}$

Again we have two methods.

(I) $\left(2 - \frac{r}{a_0}\right)\left(e^{-\frac{r}{2a_0}}\right) = 0$

$$\Rightarrow 2 - \frac{r}{a_0} = 0 \qquad \text{and} \qquad e^{-r/2a_0} = 0$$

$$\boxed{r = 2a_0} \qquad \boxed{r = \infty}$$

Hence 1 node is present and the position of node is $2a_0$

~~Example~~ (II) On compairing we get,

$$\boxed{l=0} \text{ and } \boxed{n=2}$$

Radial Node $= 2 - 0 - 1$

$= 1$ Ans.

* Finding Wave Function for 1-s orbital. for H-atom :-

We know that for H-atom ψ {wave func^n} consists of two parts, i.e. Radial Part and Angular part.

Hence,

$$\psi_{1s} = R(r) \cdot Y(\theta, \phi)$$

$$\psi_{1s} = R(n, l)\, Y(m, l)$$

For 1s orbital :-

$m = 0 \qquad l = 0 \qquad$ and $\qquad n = 1$

$$\boxed{\psi_{1s} = R(1,0)\, Y(0,0)}$$

Radial Part for 1s

We know that Radial part is given by,

$$\boxed{R_{nl} \propto \left(\frac{2Zr}{na_0}\right)^{l} e^{-\frac{Zr}{na_0}}}$$

For H-atom and 1-s orbital,

$n = 1, \quad l = 0 \quad Z = 1.$

$$R_{n,l} \propto \left(\frac{2 \times 1 \times r}{1 \times a_0}\right)^{0} e^{-\frac{1r}{na_0}}$$

$$\boxed{R_{n,l} = N e^{-r/a_0}}$$

Proportionality Constant.

We will find the value of 'N' by using condition of Normalisation.

We know that,

Condition of Normalisation $= \int \psi^* \psi \, d\tau = 1$

For H-atom,

$$d\tau = r^2 dr \sin\theta \, d\theta \, d\phi$$

But we will use only,

$$\boxed{d\tau = r^2 dr}$$ because we are considering radial part only.

Hence on applying condition of Normalisation, we have,

$$\int R^*_{1,0} \cdot R_{10} \, d\tau = 1$$

Now; $R_{10} = Ne^{-r/a_0}$ $\quad R_{10}^* = Ne^{-r/a_0}$

$$\int_0^\infty R_{10}^* R_{10} r^2 dr = 1$$

$$\int_0^\infty Ne^{-r/a} \cdot Ne^{-r/a} r^2 dr = 1$$

$$\boxed{N^2 \int_0^\infty r^2 e^{-2r/a} dr = 1} \quad \text{—(i)}$$

Using integral formulae;

$$\boxed{\int_0^\infty r^n e^{-\alpha r} dr = \frac{n!}{(\alpha)^{n+1}}}$$

In above integral we have, $n=2$ $\alpha = \frac{2}{a}$

$$N^2 \left[\frac{2!}{\left(\frac{2}{a}\right)^3} \right] = 1$$

$$N^2 \left[\frac{a^3}{4} \right] = 1$$

$$N^2 = \frac{4}{a^3}$$

$$\boxed{N = \frac{2}{(a)^{3/2}}}$$ ≐ Normalisation Constant.

Hence Radial Part for 1-s orbital is given by;

$$\boxed{R_{10} = \frac{2}{a^{3/2}} e^{-r/a_0}}$$

⊛ Angular Part for 1-s orbital:-

For 1s orbital ; $l=0$ and $m=0$.

$$Y(0,0) \propto \sin^0\theta \cos^{0-|0|}\theta \, e^{-i0\phi}$$

$$Y \propto 1$$

$$\boxed{Y(0,0) = N}$$

Note :- For any s-orbital whether 1s, 2s, 3s, 4s value of angular part will be constant.

Again Normalising angular part,

$$d\tau = r^2 dr \sin\theta d\theta d\phi$$

But for angular part,

$$\boxed{d\tau = \sin\theta d\theta d\phi} \quad \text{where} \quad \boxed{\begin{matrix} 0<\theta<\pi \\ 0<\phi<2\pi \end{matrix}}$$

On normalisation we have,

$$\int Y^*_{(l,m)} Y_{(l,m)} d\tau = 1$$

$$\int_0^{2\pi}\int_0^{\pi} Y^*_{(0,0)} Y_{(0,0)} \sin\theta \, d\theta \, d\phi = 1$$

$\boxed{\because Y = N}$ — we have finded it earlier.

$$\int_0^{2\pi}\int_0^{\pi} N \cdot N \sin\theta \, d\theta \, d\phi = 1$$

$$N^2 \int_0^{\pi} \sin\theta d\theta \int_0^{2\pi} d\phi = 1$$

$$N^2 \left[-\cos\theta\right]_0^{\pi} \left[\phi\right]_0^{2\pi} = 1$$

$$N^2 \left[-\cos\pi + \cos 0^\circ\right]\left[2\pi - 0\right] = 1$$

$$N^2 \left[1+1\right]\left[2\pi\right] = 1$$

$$N^2 4\pi = 1$$

$$\boxed{N = \sqrt{\frac{1}{4\pi}}} = \text{Normalisation Constant for Angular Part.}$$

Hence,

$$\psi_{(r,\theta,\phi)} = R(n,l)\, Y(l,m)$$

$$\psi_{1s} = R(1,0)\, Y(0,0)$$

$$\psi_{1s} = \frac{2}{(a)^{3/2}} e^{-r/a} \times \frac{1}{2\sqrt{\pi}}$$

$$\psi_{1s} = \frac{1}{\sqrt{\pi}} \times \frac{1}{a^{3/2}} \times e^{-r/a} \quad \Rightarrow \quad \boxed{\psi_{1s} = \frac{e^{-r/a}}{\sqrt{\pi}\,(a)^{3/2}}}$$

⊛ Significance of n, l, m :-

→ In calculation of Energy of nth orbit of Hydrogen and Hydrogen like atom.

$$\boxed{E_n = \frac{-13.6\, z^2}{n^2}} \text{ eV}$$

$$\boxed{E_n = \frac{-0.5\, z^2}{n^2}} \text{ a.m / Heartree}$$

$$\boxed{E_n = \frac{-R_H\, z^2}{n^2}} \text{ cm}^{-1} \qquad R_H = \text{Rydberg Constant.}$$

$$\boxed{E_n = \frac{-R_H\, h.c.z^2}{n^2}} \text{ Joule}$$

∵ In all the above forms of energy representation it is clear that energy for Hydrogenic species depends upon value of principal quantum number (n)

For H atom

$$E_n = \frac{-13.6}{n^2} \text{ eV}$$

Hence for all the hydrogenic atoms / species, energy level spacing ↓ses on ↑ing value of n.

In PIB model energy level spacing used to ↑se with ↑ing 'n'.

$n=5$ ——— $E_5 = \frac{-13.6}{25} = -0.53$ eV

$n=4$ ——— $E_4 = \frac{-13.6}{16} = -0.81$ eV

$n=3$ ——— $E_3 = \frac{-13.6}{9} = -1.51$ eV

$n=2$ ——— $E_1 = \frac{-13.6}{4} = -3.4$ eV

$n=1$ ——— $E_1 = \frac{-13.6}{1} = -13.6$ eV

* Concept of Degeneracy :-

$$\boxed{\text{Degeneracy} = n^2}$$

as from above expressions energy depends only on 'n' for Hydrogenic species.

$$\boxed{\text{Spin including degeneracy} = 2n^2}$$

Example:- $n=1$ degeneracy $= 1$ Verification = 1s $\square$

$n=2$ degeneracy $= 2^2 = 4$ Verification = 2s, 2p

$\boxed{1}$ $\boxed{2|3|4}$
2s 2p

$n=3$ degeneracy $= 3^2 = 9$ Verification

3s, 3p, 3d ⇒ $\square$ $\square\square\square$ $\square\square\square\square\square$
3s 3p 3d.

Example:- Calculate degeneracy for H-atom having energy,

$$E = \frac{-R_H}{25}$$

Compairing with,

$$E_n = \frac{-R_H Z^2}{n^2} \quad ; \text{ for H-atom } Z=1$$

$$\frac{-R_H}{n^2} = \frac{-R_H}{25} \Rightarrow \boxed{n^2 = 25}$$ Hence degeneracy is 25.

Example:- Calculate degeneracy for H-atom having energy,

$$E = -3.4\,eV$$

On Compairing we have,

$$E_n = \frac{-13.6 Z^2}{n^2} eV \; ; \text{ for H-atom } Z=1$$

$$\frac{-13.6}{n^2} = -3.4 \Rightarrow \boxed{n^2 = 4}$$ Hence degeneracy is 4.

Example:- $E_n = \frac{-e^2}{72\pi\varepsilon_0 a_0}$ for H-atom, calculate degeneracy.

Compairing with,

$$E = \frac{-e^2}{8\pi\varepsilon_0 a_0} \cdot \frac{Z^2}{n^2} \quad ; \text{ H-atom } Z=1$$

$$\frac{1}{n^2} \times \frac{-e^2}{8\pi\varepsilon_0 a_0} = \frac{-e^2}{72\pi\varepsilon_0 a_0}$$

$$\boxed{n^2 = 9}$$ Hence degeneracy is 9.

* Calculation of Total Orbital Angular Momentum :-

Orbital Angular Momentum,

$$\boxed{L_z = m\hbar}$$

Total Orbital Angular Momentum,

$$\boxed{L^2 = l(l+1)\hbar^2}$$

and we know that,

$$\boxed{L^2 = L_x^2 + L_y^2 + L_z^2}$$

GATE :- Calculate value of $L_x^2 + L_y^2 = ?$

$$L^2 = L_x^2 + L_y^2 + L_z^2$$

$$L_x^2 + L_y^2 = L^2 - L_z^2$$

$$= l(l+1)\hbar^2 - m^2\hbar^2$$

$$\boxed{L_x^2 + L_y^2 = \hbar^2[l(l+1) - m^2]}$$

* Plotting graphs for different Probability :-

We know that,

$$\boxed{P = \int_a^b \psi^* \psi \, d\tau}$$

Since we are considering radial part only and for s-orbitals i.e. $m=0$, $l=0$ and $n=1, 2, 3 \ldots\ldots$

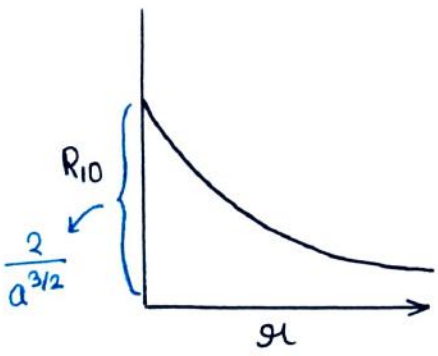
$$P = \int R_{nl} R^*_{nl} \, r^2 dr$$

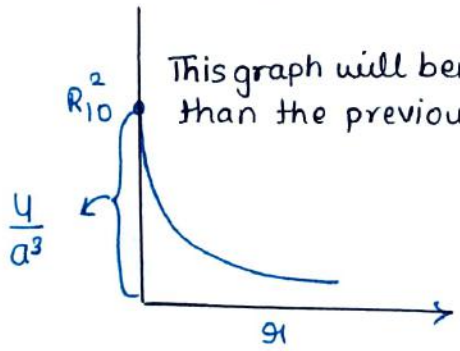
$$\boxed{P = \int R_{nl}^2 \, r^2 \, dr}$$ where $\boxed{R_{nl}^2 r^2 = \text{RDF (Radial Distributive func}^n\text{)}}$

For 1s :-

$$R_{10} = \frac{2}{(a)^{3/2}} e^{-r/a}$$

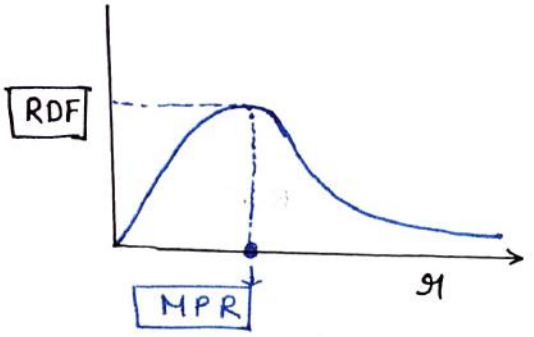
$$R_{10}^2 = \frac{4}{a^3} e^{-2r/a}$$





This graph will bend more than the previous one.

* R.D.F. for 1s = $r^2 R_{10}^2 = \frac{4}{3} e^{-2r/a} r^2$.



Most probable Radius = a_0

<u>How to calculate MPR :-</u>

By applying maxima-minima condition, we can find MPR.

$$\frac{d}{dr} RDF = 0 \quad \text{where} \quad RDF = \frac{4}{a^3} r^2 e^{-2r/a_0}$$

$$\Rightarrow \quad \frac{d}{dr}\left(\frac{4}{a^3} r^2 e^{-2r/a_0}\right) = 0$$

$$\frac{4}{a^3} \frac{d}{dr} r^2 e^{-2r/a_0} = 0$$

$$\frac{4}{a^3}\left\{ r^2\left(\frac{-2}{a}\right) e^{-2r/a} + e^{-2r/a} \cdot 2r \right\} = 0$$

$$\frac{4}{a^3} r e^{-2r/a} \left\{ -\frac{2r}{a} + 2 \right\} = 0$$

Now we have,

(i) $r = 0$ (boundary)

(ii) $e^{-2r/a} = 0$, $r = \infty$ (boundary)

Not possible for MPR

(iii) $-\frac{2r}{a} + 2 = 0$

$\boxed{r = a_0}$

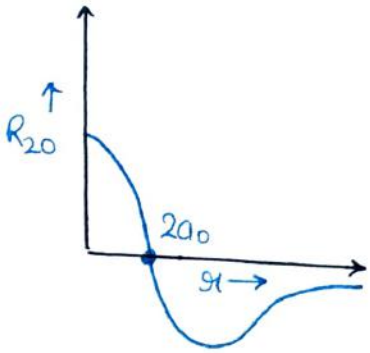
Hence MPR for 1s = a_0. → Bohr Radius.

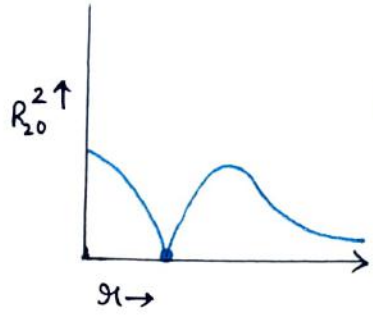
iii) For 2-s orbital :-

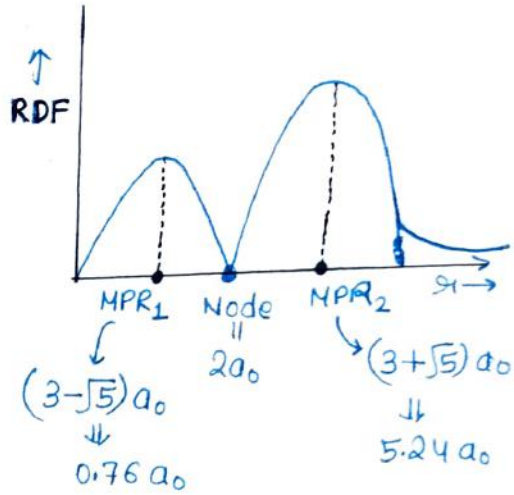
Radial Part ; $R_{20} = N\left\{2 - \frac{r}{a^0}\right\} e^{-r/2a_0}$

∵ Remember 1 radial node is also present at $r = 2a_0$. We have calculated it earlier.

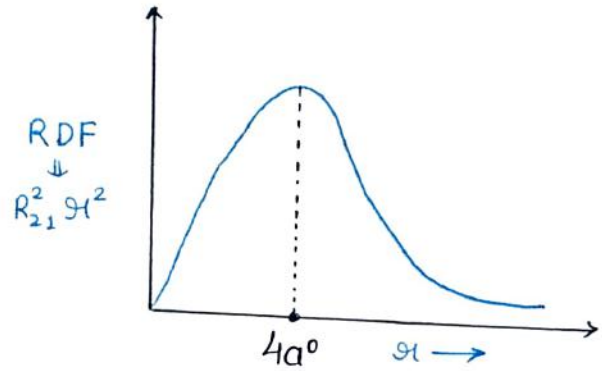
$RDF = R_{20}^2 r^2$







iii) For 2p orbital :-



Note :- If on finding the wave function for a given orbital, our radial part comes out nodeless, then we have a direct formulae for the calculation of MPR.

$$\boxed{MPR = \frac{n^2 a_0}{Z}}$$

For H-atom ; $Z = 1$

1s	$n-l-1 = 1-1 = 0$ Node	$MPR = a_0$
2p	$n-l-1 = 2-1-1 = 0$ Node	$MPR = (2)^2 a_0 = 4a_0$
3d	$n-l-1 = 3-2-1 = 0$ Node	$MPR = (3)^2 a_0 = 9a_0$
4f	$n-l-1 = 4-3-1 = 0$ Node	$MPR = (4)^2 a_0 = 16a_0$

⊛ Average Value Results for H-atom :-

$\langle x \rangle = 0$ $\quad$ $\langle y \rangle = 0$ $\quad$ $\langle z \rangle = 0$

$$\langle r \rangle = \frac{a_0}{Z}\left[\frac{3}{2}n^2 - \frac{l(l+1)}{2}\right] \qquad \langle r^2 \rangle = \frac{n^2 a_0^2}{2Z^2}\left[5n^2 - 3l(l+1) + 1\right]$$

$$\left\langle \frac{1}{r} \right\rangle = \frac{Z}{a_0 n^2} \qquad \left\langle \frac{1}{r^2} \right\rangle = \frac{Z^2}{a_0^3 n^3 \left(\frac{l+1}{2}\right)}$$

$$\langle K.E. \rangle = \frac{-\hbar^2}{2ma^2} \qquad \langle P.E. \rangle = \frac{-Ze^2}{4\pi\varepsilon_0 a^0}$$

Example :- Calculate $\langle r \rangle$ for 1s-orbital. H atom,

$Z = 1 \quad n = 1 \quad l = 0$

$$\langle r \rangle = \frac{a_0}{Z}\left[\frac{3}{2}n^2 - \frac{l(l+1)}{2}\right] = \frac{a_0}{1}\left[\frac{3}{2} \times 1 - 0\right]$$

$$\boxed{\langle r \rangle = 1.5\, a_0} \qquad \boxed{\langle r^2 \rangle = 3a_0^2} \qquad \boxed{\left\langle \frac{1}{r} \right\rangle = \frac{1}{a_0}}$$

* Uncertainity Concept

$$\boxed{\text{Uncertainity } (\Delta m) = \sqrt{\langle m^2 \rangle - \langle m \rangle^2}}$$

Example :- Find uncertainity in 'r' for 1s-orbital in H-atom.

$$\Delta r = \sqrt{\langle r^2 \rangle - \langle r \rangle^2}$$

We have already calculated $\langle r \rangle$ and $\langle r^2 \rangle$

$$\Delta r = \sqrt{3a_0^2 - \left(\frac{3}{2}a_0\right)^2}$$

$$\Delta r = \sqrt{3a_0^2 - \frac{9}{4}a_0^2} = \sqrt{\left(\frac{12-9}{4}\right)a_0}$$

$$\Delta r = \sqrt{\frac{3a_0^2}{4}}$$

$$\boxed{\Delta r = \frac{\sqrt{3}}{2}a_0}$$

For H-atom :-

$$\langle P_r \rangle = 0$$

$$\langle P_r^2 \rangle = \frac{\hbar^2}{a^2}.$$

$\because$ $\langle K.E. \rangle = \dfrac{\hbar^2}{2ma^2}$ —(i)

and $K.E. = \dfrac{P_r^2}{2m}$ —(ii)

from (i) and (ii) $\dfrac{P_r^2}{2m} = \dfrac{\hbar^2}{2ma^2}$

$$\boxed{P_r^2 = \frac{\hbar^2}{a^2}}$$

Uncertainity in Momentum,

$$\Delta P_r = \sqrt{\langle P_r^2 \rangle - \langle P_r \rangle^2}$$

$$\Delta P_r = \sqrt{\frac{\hbar^2}{a^2} - 0} = \frac{\hbar}{a}$$

$$\boxed{\Delta P_r = \frac{\hbar}{a}}$$

* Some Important Integrations:-

i) $\displaystyle\int_0^\infty r^n e^{-\alpha r}\, dr = \frac{n!}{(\alpha)^{n+1}} = \frac{n!}{(\alpha)^{n+1}}$

ii) $\displaystyle\int_0^\pi \sin^3\theta\, d\theta = \frac{4}{3}$

iii) $\displaystyle\int_0^\pi \cos^2\theta \sin\theta\, d\theta = \frac{2}{3}$

iv) $\displaystyle\int_0^\pi \sin\theta \cos\theta\, d\theta = 0$

These integrations will be required during normalisation of wave func^n.

Example :- Find whether the wave function,

$$\psi = e^{-r}\cos\theta \quad \text{is normalised?}$$

Sol^n:- We know that for Normalisation;

$$\int \psi^* \psi\, d\tau = 1$$

$$\Rightarrow \int e^{-r}\cos\theta \cdot e^{-r}\cos\theta\, d\tau$$

for H-atom ; $d\tau = r^2 dr \sin\theta\, d\theta\, d\phi$.

$$\int_0^{2\pi}\int_0^{\pi}\int_0^{\infty} e^{-2r}\cos^2\theta\, r^2 dr\, d\theta \sin\theta\, d\phi$$

$$= \int_0^{\infty} e^{-2r}\cdot r^2 dr \int_0^{\pi} \sin\theta \cos^2\theta\, d\theta \int_0^{2\pi} d\phi$$

$$= \frac{2!}{(2)^3} \times \frac{2}{3} \times 2\pi$$

$$= \frac{\pi}{3} \qquad \because \int \psi^*\psi\, d\tau \neq 1$$

Hence given wave func^n is not Normalised.

Normalisation Constant $= \sqrt{\frac{3}{\pi}}$

Hence,

Normalised Wave Function $= \sqrt{\frac{3}{\pi}}\, e^{-r}\cos\theta$.

Example :- Find whether wave function,

$\psi = e^{-r}\sin\theta$ is normalised ?

Sol^n, Again we will have.

$$\int_0^{\infty} e^{-2r} r^2 dr \int_0^{\pi} \sin^3\theta\, d\theta \int_0^{2\pi} d\phi$$

$$= \frac{2!}{2^3} \times \frac{4}{3} \times 2\pi$$

$$= \frac{2\pi}{3}$$; Again wave function is not normalised.

$$N.C. = \sqrt{\frac{3}{2\pi}}$$

$$\boxed{\psi_{new} = \sqrt{\frac{3}{2\pi}}\, e^{-r}\sin\theta}$$

⊛ Average Values in case of PIB Model :-

We know that in PIB model average values are calculated by,

$$\langle x \rangle = \int \psi^* x \psi \, dx.$$

Some Results :- $\langle x \rangle = \frac{l}{2}$ and $\langle x^2 \rangle = \frac{l^2}{3} - \frac{l^2}{2n^2\pi^2}$

Uncertainity in Position :-

$$\Delta x = \sqrt{\langle x^2 \rangle - \langle x \rangle^2}$$

$$= \sqrt{\frac{l^2}{3} - \frac{l^2}{2n^2\pi^2} - \frac{l^2}{4}} = \sqrt{\frac{l^2}{3} - \frac{l^2}{4} - \frac{l^2}{2n^2\pi^2}}$$

$$\Delta x = \sqrt{\frac{l^2}{12} - \frac{l^2}{2n^2\pi^2}} \qquad \boxed{\Delta x = l\sqrt{\frac{1}{12} - \frac{1}{2n^2\pi^2}}}$$

for ground state ie $n=1$

$$\boxed{\Delta x = l\sqrt{\frac{1}{12} - \frac{1}{2\pi^2}}}$$

Results on Momentum :-

$$\langle P_x \rangle = 0 \qquad \text{and} \qquad \langle P_x^2 \rangle = \frac{n^2h^2}{4l^2}$$

In PIB model,

$$\langle K.E. \rangle = \frac{n^2 h^2}{8ml^2}$$

and

$$\langle K.E. \rangle = \frac{P_x^2}{2m}$$

$$\Rightarrow P_x^2 = 2m \times \frac{n^2h^2}{8ml^2} = \frac{n^2h^2}{4l^2}$$

$$\boxed{P_x^2 = \frac{n^2h^2}{4l^2}}$$

Uncertainity in Momentum :-

$$\Delta P_x = \sqrt{\langle P_x^2 \rangle - \langle P_x \rangle^2}$$

$$= \sqrt{\frac{n^2h^2}{4l^2} - (0)^2}$$

$$\boxed{\Delta P_x = \frac{nh}{2l}}$$

SIMPLE HARMONIC OSCILLATOR

We have to study SHO in 3-parts,

1-D SHO 2-D SHO 3-D SHO

1-D SHO :-

We know that Schrodinger equation is given by:

$$\boxed{\nabla^2\psi + \frac{2m}{\hbar^2}[E-V]\psi = 0} \quad \text{and} \quad \boxed{V = \frac{1}{2}Kx^2}$$

$$\Rightarrow \quad \frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}\left[E - \frac{1}{2}Kx^2\right]\psi = 0$$

$$\frac{d^2\psi}{dx^2} + \left\{\frac{2mE}{\hbar^2} - \frac{mKx^2}{\hbar^2}\right\}\psi = 0$$

Let $\boxed{\alpha = \frac{2mE}{\hbar^2}}$ and $\boxed{\beta = \frac{mK}{\hbar^2}}$

$$\frac{d^2\psi}{dx^2} + \left\{\alpha - \beta^2x^2\right\}\psi = 0 \quad \text{——— (i)}$$

On solving equation (i), we have our final expression.

$$\boxed{\psi_n(\xi_1) = \left(\frac{1}{2^n n!}\right)^{1/2}\left(\frac{\beta}{\pi}\right)^{1/4} H_n(\xi_1)\, e^{-\frac{\xi_1^2}{2}}}$$

In SHO, $n = 0, 1, 2, 3, \ldots\ldots$

and $\boxed{(\xi_1) = \sqrt{\beta}\,x}$

when,

$n=0 \quad H_0(\xi_1) = 1$

$n=1 \quad H_1(\xi_1) = 2\xi_1 = 2\sqrt{\beta}\,x$

$n=2 \quad H_2(\xi_1) = 4\xi_1^2 - 2 = 4\beta x^2 - 2.$

Note:-

When, $H_{n \to even} = (x)^{even}$

$H_{n \to odd} = (x)^{odd}$

* Now for ground state, $n=0$.

$$\psi_0(\xi) = \left(\frac{1}{2^0\, 0!}\right)\left(\frac{\beta}{\pi}\right)^{1/4} H_0(\xi)\, e^{-\frac{\xi^2}{2}}$$

$$\boxed{\psi_0 = \left(\frac{\beta}{\pi}\right)^{1/4} e^{-\frac{\beta x^2}{2}}}$$

Hence we can reduce eq^n for wave func^n as,

$$\boxed{\psi_n = N H_n(\xi)\, e^{-\frac{\xi^2}{2}}}$$

In terms of 'x'

$$\boxed{\psi_n = N H_n(x)\, e^{-\frac{\beta x^2}{2}}}$$

n=even $\quad$ n=odd

x^{even} $\quad$ x^{odd}

N= Normalisation constant.

Now,

SHO in ground state i.e. $n=0$.

$$\boxed{\psi_0 = \left(\frac{\beta}{\pi}\right)^{1/4} e^{-\frac{\beta x^2}{2}}}$$

when $n=1$;

$$\boxed{\psi_1 = N \cdot x\, e^{-\frac{\beta x^2}{2}}}$$

* Energy Calculation:-

In order to evaluate the energy expression in SHO, we will use the relation,

$$\boxed{\frac{\alpha}{\beta} = (2n+1)}$$

where $\alpha = \dfrac{2mE}{\hbar^2}$

$$\beta = \frac{\sqrt{mK}}{\hbar^2}$$

$$\frac{\frac{2mE}{\hbar^2}}{\frac{\sqrt{mK}}{\hbar}} = (2n+1) \Rightarrow \frac{2\sqrt{m}E}{\hbar\sqrt{K}} = 2n+1.$$

$$E = \frac{(2n+1)}{\sqrt{m}\cdot 2} \times \hbar\sqrt{K} \Rightarrow E = \frac{(n+1/2)}{\sqrt{m}}\hbar\sqrt{K}$$

$$\boxed{E = \left(n+\frac{1}{2}\right)\hbar\sqrt{\frac{K}{m}}}$$ and $\hbar = \frac{h}{2\pi}$

$$\boxed{E = \left(n+\frac{1}{2}\right)\frac{h}{2\pi}\sqrt{\frac{K}{m}}}$$ and from spectroscopy,

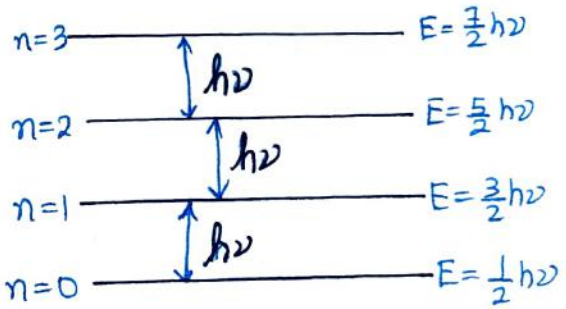
$$\nu(\text{frequency}) = \frac{1}{2\pi}\sqrt{\frac{K}{m}}$$

$$\boxed{E = \left(n+\frac{1}{2}\right)h\nu} \longrightarrow \star$$

$\star$ is the required expression for the energy in 1-D SHO.

* Energy Levels:

In vibrational SHO, spacing b/w energy level is constant.



* Normalising the wave function:-

Limits used during integration $[-\infty, \infty]$

We will use integration of the type,

$$\int_{-\infty}^{\infty} x^n e^{-\beta x^2}\,dx \begin{cases} \xrightarrow{n=\text{even}} \dfrac{\Gamma\left(\frac{n+1}{2}\right)}{\beta^{\frac{n+1}{2}}} \\ \xrightarrow{n=\text{odd}} 0 \end{cases}$$

Note: $\Gamma\left(\frac{1}{2}\right) = \sqrt{\pi}$

$\Gamma\left(\frac{3}{2}\right) = \frac{1}{2}\sqrt{\pi}$

$\Gamma\left(\frac{5}{2}\right) = \frac{3}{2}\times\frac{1}{2}\sqrt{\pi}$

$\Gamma\left(\frac{7}{2}\right) = \frac{5}{2}\times\frac{3}{2}\times\frac{1}{2}\sqrt{\pi}$

Now; Wave function for SHO is given by,

$$\psi = Ne^{-\frac{\beta x^2}{2}}$$

We know that condition of normalisation is given by;

$$\int \psi^* \psi \, d\tau = 1$$

$$\int_{-\infty}^{\infty} Ne^{-\beta\frac{x^2}{2}} \cdot Ne^{-\beta\frac{x^2}{2}} \, dx = 1$$

$$N^2 \int_{-\infty}^{\infty} e^{-\beta x^2} dx = 1$$

$$N^2 \int_{-\infty}^{\infty} (x)^0 e^{-\beta x^2} dx = 1$$

Comparing above integration with

$$\int_{-\infty}^{\infty} x^n e^{-\beta x^2} dx = \frac{\Gamma\frac{n+1}{2}}{\beta^{\frac{n+1}{2}}}$$

We have, $n=0$ (even)

$$N^2 \int_{-\infty}^{\infty} (x)^0 e^{-\beta x^2} = 1$$

$$\frac{N^2 \Gamma\frac{0+1}{2}}{\beta^{0+1/2}} = 1$$

$$N^2 \frac{\Gamma\frac{1}{2}}{\beta^{1/2}} = 1$$

$$N^2 \sqrt{\frac{\pi}{\beta}} = 1$$

$$N^2 = \sqrt{\frac{\beta}{\pi}}$$

$$\boxed{N = \left(\frac{\beta}{\pi}\right)^{1/4}}$$

Hence our new wave func^n becomes.

$$\boxed{\psi(x) = \left(\frac{\beta}{\pi}\right)^{1/4} e^{-\beta\frac{x^2}{2}}}$$

* Plotting Graph :-

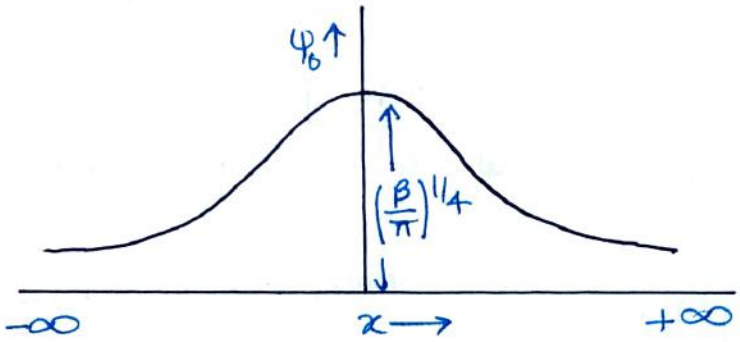
Boundary Conditions = $(-\infty, \infty)$

$$\boxed{\psi_0 = \left(\frac{\beta}{\pi}\right)^{1/4} e^{-\frac{\beta x^2}{2}}}$$

$\left.\begin{array}{l} x = -\infty \\ \text{and} \\ x = \infty \end{array}\right\} \rightarrow \psi_0 = 0$ as $e^{-\infty} = 0$

and

at $x=0$ $\quad \psi_0 = \left(\frac{\beta}{\pi}\right)^{1/4}$



Hence,

max value of $\psi(x)$ is at $x=0$.

<u>Now,</u>

$$\psi(x) = N e^{-\frac{\beta x^2}{2}} \quad \text{and} \quad \psi(-x) = N e^{-\frac{\beta x^2}{2}}$$

$$\Rightarrow \boxed{\psi(x) = \psi(-x)}$$

Hence wave function $\psi_0(x)$ for SHO at $n=0$ (ground state) is a "Symmetric Wave Function".

<u>Now;</u> $\psi_1(x)$ for SHO ie. $n=1$

$$\psi_1 = \underbrace{\left(\frac{\beta}{\pi}\right)^{1/4} \sqrt{2\beta}}_{=N} x\, e^{-\frac{\beta x^2}{2}}$$

$$\boxed{\psi_1 = N x e^{-\frac{\beta x^2}{2}}}$$

at Boundary $[-\infty, \infty]$

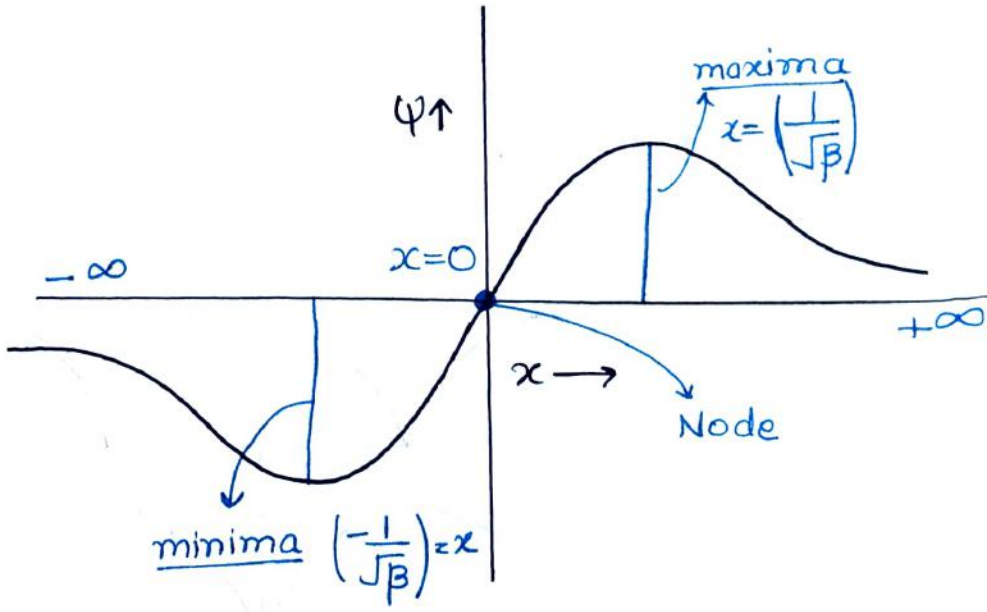
$x = \infty$ or $-\infty$

$e^{-\infty} = 0$

$$\Rightarrow \boxed{\psi_1(x) = 0}$$

at $x=0$

$$\boxed{\psi_1(x) = 0}$$



$\because$ $x=0$ is not boundary condition hence we will have 1 node.

Now,

$$\psi_1(x) = N x e^{-\frac{\beta x^2}{2}} \quad \text{and} \quad \psi_1(-x) = -N x e^{-\beta \frac{x^2}{2}}$$

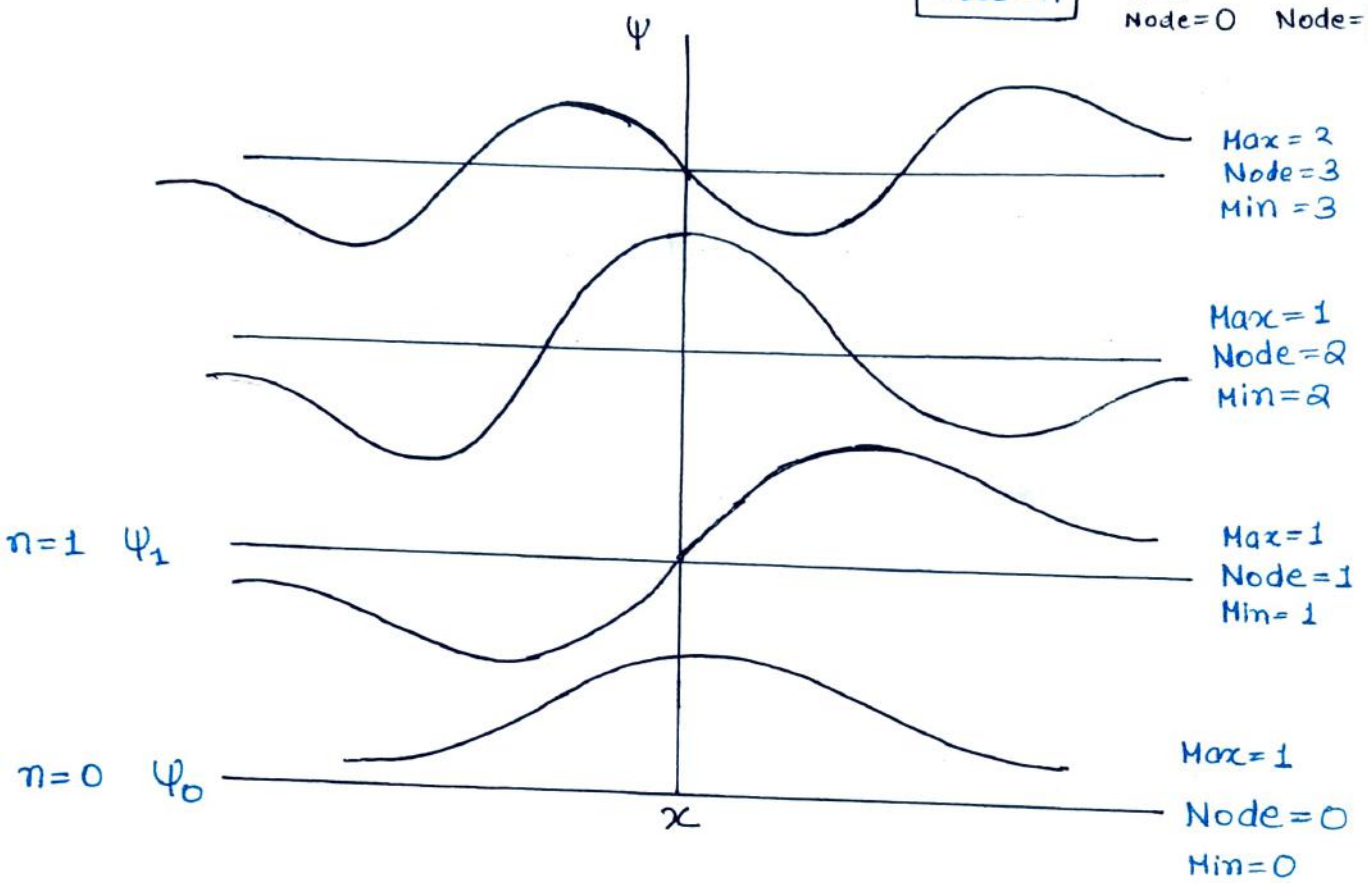
Hence, $\boxed{\psi_1(x) = -\psi_1(x)}$

Hence for $n=1$, SHO will have Antisymmetric function.

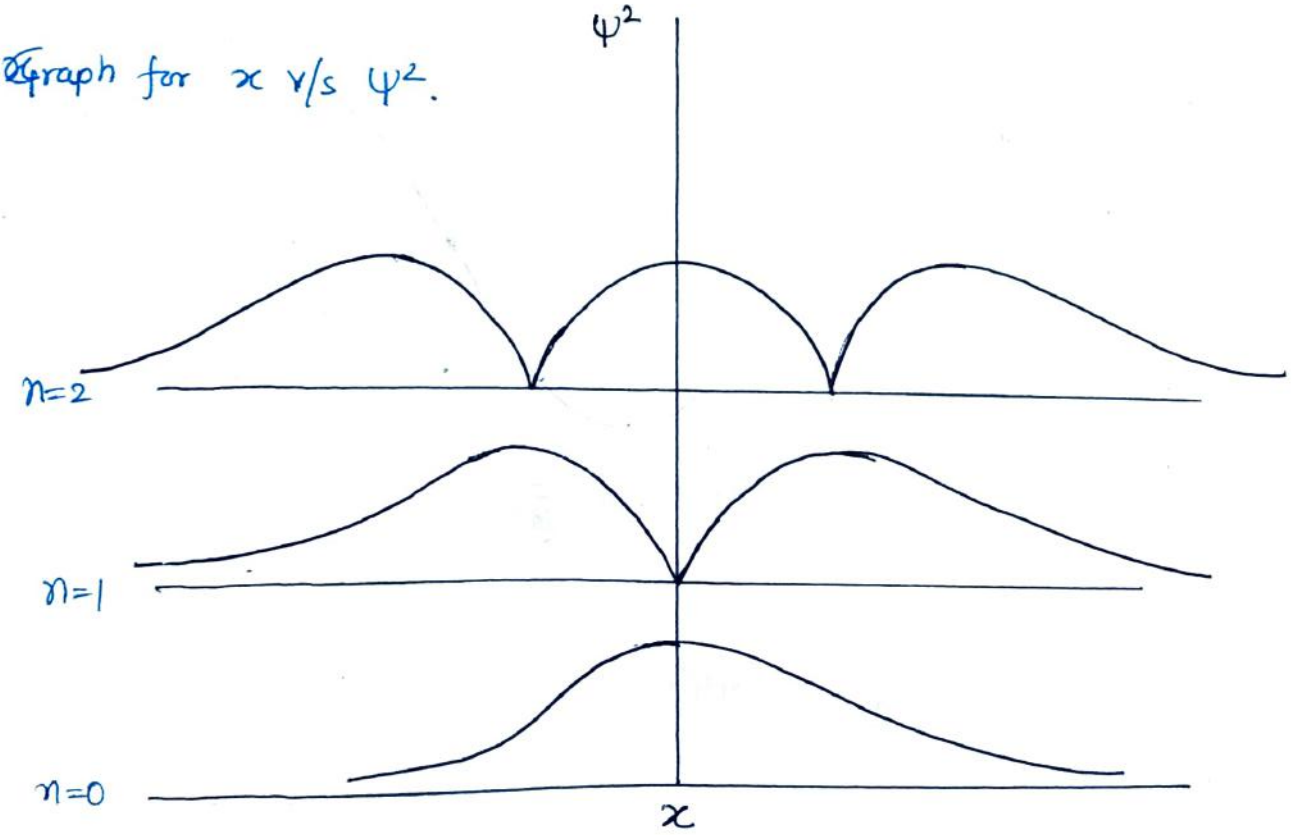
* Combining All Graphs :-

Hence, General formulae for Node,

$\boxed{\text{Node} = n}$ $n=0$ Node $=0$ $n=1$ Node $=1$.



Graph for x v/s ψ^2.



* Average Value Result :-

(i) $\langle x \rangle = 0$ (ii) $\langle P_x \rangle = 0$ (iii) $\langle x^2 \rangle = \left(n+\frac{1}{2}\right)\frac{1}{\beta}$

(iv) $\langle P_x^2 \rangle = \left(n+\frac{1}{2}\right)\beta\hbar^2$

{ Note $\underbrace{\langle x \rangle = 0 \text{ and } \langle P_x \rangle = 0}_{\text{for all values of } (n) \text{ is SHO}}$ }

Example :- Find $\langle x \rangle$ for $n=0$ in SHO.

Sol^n $\langle x \rangle = 0$ $\langle P_x \rangle = 0$ $\langle x^2 \rangle = \frac{1}{2\beta}$ $\langle P_x^2 \rangle = \frac{1}{2}\beta\hbar^2$

Example :- Calculate uncertainity in position in ground state for SHO.

Sol^n: Ground state $\Rightarrow n=0$.

$$\Delta x = \sqrt{\langle x^2 \rangle - \langle x \rangle^2}$$

$$\Delta x = \sqrt{\frac{1}{\beta} - 0} \Rightarrow \boxed{\Delta x = \frac{1}{\sqrt{\beta}}} \text{ and } \boxed{\beta = \frac{\sqrt{mK}}{\hbar}}$$

Example :- Calculate uncertainity in momentum.

$$\Delta P_x = \sqrt{\langle P_x^2 \rangle - \langle P_x \rangle^2} = \sqrt{\frac{1}{2}\beta\hbar^2 - 0} = \sqrt{\frac{\beta}{2}}\hbar$$

$$\boxed{\Delta P_x = \sqrt{\frac{\beta}{2}}\hbar}$$

* Comparison between classical and quantum mechanical SHO.

→ From the Graph for ψ v/s x and $|\psi^2|$ v/s x, it is clear that particle spend more time at eqb ($x=0$) in the ground state because function is maximum at ($x=0$).

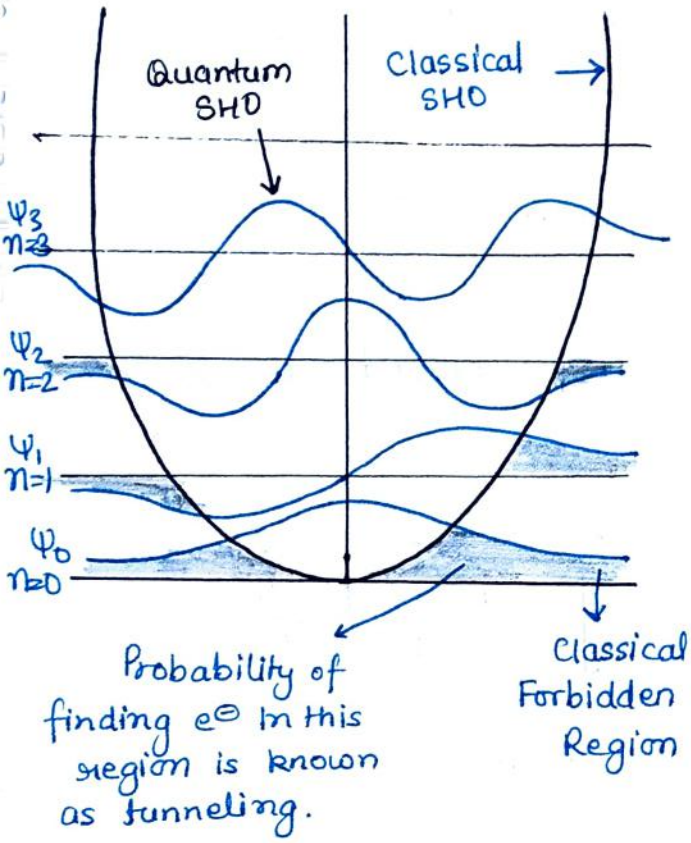
→ But in classical SHO, particle spend minimum time at eqb, $x=0$.

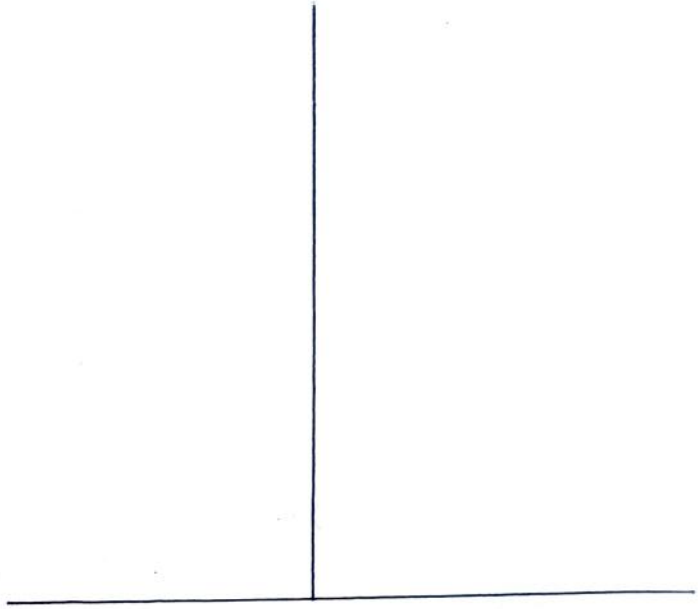
→ In classical, K.E. or P.E. can be zero but in quantum neither K.E. can be zero nor P.E.

→ In classical SHO particle have finite amplitude vibration but in quantum the particle can be found anywhere from $-\infty$ to $+\infty$. Therefore particle can also be found in classical forbidden region and this phenomenae is known as tunneling.

→ Tunneling decreases as value of (n) increases.

Bohr's Correspondance Principle :- At higher value of 'n', quantum mechanics approaches to classical mechanics.





⊛ 2-D SHO :-

It is classified into two categories;

(1) Isotropic $\Rightarrow \nu_x = \nu_y = \nu$ i.e. ν_x = frequency along 'x' axis.
ν_y = frequency along 'y' axis.

(2) Anisotropic $\Rightarrow \nu_x \neq \nu_y$.

∵ Wave functions are multiplicative in nature.

$$\boxed{\psi = \psi_x \cdot \psi_y}$$

For Anisotropic

and $$\psi_{(x,y)} = \left(\frac{\beta}{\pi}\right)^{1/4} e^{-\frac{\beta x^2}{2}} \left(\frac{\beta}{\pi}\right)^{1/4} e^{-\frac{\beta y^2}{2}}$$

also for isotropic

∵ Energy is additive in nature.

$$\boxed{E_{2D} = \left(n_x + \frac{1}{2}\right) h\nu_x + \left(n_y + \frac{1}{2}\right) h\nu_y}$$ = For Anisotropic.

<u>For isotropic</u>; $\nu_x = \nu_y = \nu$.

$$E_{2D} = \left(n_x + \frac{1}{2}\right) h\nu + \left(n_y + \frac{1}{2}\right) h\nu$$

$$E_{2D} = \left(n_x + n_y + \frac{1}{2} + \frac{1}{2}\right) h\nu$$

$$\boxed{E_{2D} = (n_x + n_y + 1) h\nu}$$

* <u>Concept of degeneracy</u> :-

We know that,

$$\boxed{E_{2D} = (n_x + n_y + 1) h\nu}$$

(1,2)	(2,1)	(3,0)	(0,3)	$E = 4h\nu$	$g=4$
(1,1)	(2,0)	(0,2)		$E = 3h\nu$	$g=3$
(1,0)	(0,1)			$E = 2h\nu$	$g=2$
(0,0)				$E = h\nu$	$g=1$

* <u>Trick</u> ;

If we have Energy in form of, $E = nh\nu$

Then, $\boxed{g = n}$

↳ degeneracy.

⊛ 3-D SHO :-

These are also classified into two categories;

(1) Anisotropic (2) Isotropic.

∵ Functions are multiplicative in nature.

$$\boxed{\psi_{(x,y,z)} = \psi_{(x)} \cdot \psi_{(y)} \cdot \psi_{(z)}}$$

$$\boxed{\psi_{(x,y,z)} = \left(\frac{\beta}{\pi}\right)^{1/4} e^{-\frac{\beta x^2}{2}} \left(\frac{\beta}{\pi}\right)^{1/4} e^{-\frac{\beta y^2}{2}} \left(\frac{\beta}{\pi}\right)^{1/4} e^{-\frac{\beta z^2}{2}}}$$

For isotropic 3-D SHO :-

$$E_{3D} = E_{(n_x, n_y, n_z)} = \left(n_x + \frac{1}{2}\right)h\nu + \left(n_y + \frac{1}{2}\right)h\nu + \left(n_z + \frac{1}{2}\right)h\nu$$

$$\boxed{E_{3D} = \left(n_x + n_y + n_z + \frac{3}{2}\right)h\nu}$$

* Concept of Degeneracy :-

$$E_{3D} = \left(n_x + n_y + n_z + \frac{3}{2}\right)h\nu$$

(1,0,1) (1,1,0) (0,1,1) (2,0,0) (0,2,0) (0,0,2) $E = \frac{7}{2}h\nu$ $g=6$

(1,0,0) (0,1,0) (0,0,1) $E = \frac{5}{2}h\nu$ $g=3$

(0,0,0) $E = \frac{3}{2}h\nu$ $g=1$

General formulae for Degeneracy :-

$$\boxed{g = \frac{(n+1)(n+2)}{2}} \quad \text{where} \quad \boxed{n = n_x + n_y + n_z}$$

Ex :- Calculate 'g' for $E = \frac{7}{2}h\nu$

$E = \frac{7}{2}h\nu$ and $E = \left(\underbrace{n_x + n_y + n_z}_{} + \frac{3}{2}\right)h\nu$

$E = \left(n + \frac{3}{2}\right)h\nu$

$\Rightarrow \frac{7}{2}h\nu = \left(n + \frac{3}{2}\right)h\nu$

$n = \frac{7}{2} - \frac{3}{2} = 2$

$g = \frac{(2+1)(2+2)}{2}$

$g = \frac{12}{2}$

$\boxed{g=6}$ Ans.

Ex :- Calculate 'g' for $E = \frac{13}{2}h\nu$

$E = \frac{13}{2}h\nu$ and $E = \left(n + \frac{3}{2}\right)h\nu$

$n = \frac{13}{2} - \frac{3}{2}$ $\quad g = \cancel{(5+1)}$ $\quad g = \frac{(5+1)(5+2)}{2}$

$\boxed{n=5}$ $\quad g = \frac{42}{2} = 21$ Ans

:- Rigid Rotor :-

Rigid rotor is proposed corresponding to study of rotational motion of microscopic particle.

$$\text{Rigid Rotor} = \{ \overset{\text{fixed}}{r}, \theta, \underset{[0, 2\pi]}{\phi} \}$$

and Hamiltonian operator (Energy operator in Quantum) $\hat{H}$ is given by,

$$\boxed{\hat{H} = \frac{L^2}{2I}}$$

<u>Now</u>;

$$\hat{H}\psi = \frac{L^2}{2I}\psi$$

$$\hat{H}\psi = \frac{L(L+1)}{2I}\hbar^2\psi \Rightarrow \boxed{E = \frac{L(L+1)\hbar^2}{2I}}$$

Here we replace 'L' with 'J'

$$\boxed{E = \frac{J(J+1)\hbar^2}{2I}}$$ where $J = 0, 1, 2, 3, \ldots\ldots$

Rotational Quantum Number.

$$E_J = \frac{J(J+1)}{2I}\left(\frac{h}{2\pi}\right)^2$$

$$E_J = J(J+1)\frac{h^2}{8\pi I^2}$$

$$\boxed{E_J = BJ(J+1)}$$ where $$\boxed{B = \frac{h^2}{8\pi I^2}}$$

* Concept of degeneracy :-

$$\boxed{g_n = 2J+1}$$

Now, $E = \frac{10\hbar^2}{I}$

Compairing with $E = \frac{J(J+1)\hbar^2}{2I}$ we have.

$$\frac{10\hbar^2}{I} = \frac{J(J+1)\hbar^2}{2I}$$

$$\Rightarrow \quad J^2 + J - 20 = 0$$

$$\Rightarrow \quad J^2 + 5J - 4J - 20 = 0$$

$$J(J+5) - 4(J+5) = 0$$

$$(J-4)(J+5) = 0$$

$$\boxed{J = 4 \text{ and } -5}$$

$\because$ J starts from $0, 1, 2, 3$.

$\Rightarrow \boxed{J \neq -5}$

Hence, $J = 4$.

degeneracy, $g_n = 2J + 1$

$$g_n = 2 \times 4 + 1$$

$$\boxed{g_n = 9}$$

* Normalisation of Wave Function.

$$\psi = N e^{im\phi}$$

$m = 0, \pm 1, \pm 2, \pm 3, \pm 4, \pm \ldots$

or

$m = 0, \pm 1, \pm 2, \pm 3, \pm 4, \pm \ldots\ldots$

On applying condⁿ of normalisation we have,

$$\int \psi^* \psi \, d\tau = 1$$

$$\int_0^{2\pi} N e^{im\phi} \cdot N e^{-im\phi} \, d\phi = 1$$

$$\int_0^{2\pi} N^2 \, d\phi = 1$$

$$N^2 \int_0^{2\pi} d\phi = 1$$

$$N^2 \left[\phi\right]_0^{2\pi} = 1$$

$$2\pi N^2 = 1$$

$$N^2 = \frac{1}{2\pi} \quad \Rightarrow \quad \boxed{N = \frac{1}{\sqrt{2\pi}}}$$

Hence normalised wave function will be given by,

$$\boxed{\psi = \frac{1}{\sqrt{2\pi}} e^{im\phi}}$$

* Comparison of Energy in different systems.

For Box ; $E_n = \frac{n^2 h^2}{8ml^2}$ and $n = 1, 2, 3, 4, \ldots\ldots\ldots$

H-atom ; $E_n = -\frac{13.6 Z^2}{n^2}$ and $n = 1, 2, 3, 4, \ldots\ldots\ldots$

SHO ; $E = \left(n + \frac{1}{2}\right) h\nu$ and $n = 0, 1, 2, 3, \ldots\ldots$

Rigid Rotor ; $E = \frac{J(J+1)\hbar^2}{2J}$ and $J = 0, 1, 2, 3, \ldots$

Only rigid rotor is the system having energy $(E) = 0$ in its ground state.

For Rigid Rotors and PIB Model } $V = 0$ inside

For H-atom and SHO } $V \neq 0$.

* Virial Theorem :-

$$\boxed{2T = BV}$$

where,

T = Kinetic Energy

V = Potential Energy

B = Fixed Value (Depends upon type of system).

(1) For SHO

$B = 2$.

$2T = 2V$

$T = V$

$\Rightarrow$ Kinetic Energy = Potential energy.

Energy of a SHO is given by,

$$E = \left(n + \frac{1}{2}\right) h\nu$$

Now, Total Energy = Kinetic energy + Potential Energy

and for SHO, $\boxed{KE = PE}$

$$T.E. = K.E. + K.E$$

$$KE = PE = \frac{T.E.}{2}$$

$$\Rightarrow \boxed{K.E. = \frac{\left(n+\frac{1}{2}\right)h\nu}{2}} \quad \text{and} \quad \boxed{P.E. = \frac{\left(n+\frac{1}{2}\right)h\nu}{2}}$$

<u>In case of H-atom :-</u>

For H-atom, $B = -1$.

$$2T = BV$$

$$\boxed{2T = -V} \Rightarrow \quad 2\,K.E. = -PE.$$

<u>Now;</u>

$$E = KE + PE$$

$$\boxed{E = -KE} \quad \text{and} \quad \boxed{E = \frac{PE}{2}}$$